AMERICAN

CHEMICAL JOURNAL

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THE PREPARATION OF CELLS FOR THE MEASUREMENT OF HIGH OSMOTIC PRESSURES.

By H. N. Morse and J. C. W. Frazer.

In an article describing "The Preparation of Osmotic Membranes by Electrolysis,"[1] the following opinion was expressed: "It seems improbable that the total osmotic pressᵉ of concentrated solutions, *e. g.*, molecular normal ones, wᵢₗl ever be directly measured." The results of further work in this field have led to a revision of that judgment. It has been found that a much more satisfactory membrane can be made by electrolysis than was anticipated when the first communication on the subject was written. At that time pressures of 4.5 atmospheres had been reached. The inability to attain to higher pressures was due, as was then explained, not to the weakness of the membranes, but to the impossibility, with the means employed up to that time, of securing the manometer in the cell. With improved arrangements for securing the manometer, and with such alterations of cell con-

[1] This Journal, **26**, 80.

struction as our later experience has shown us to be necessary, we have attained to a pressure of about 31.5 atmospheres with a normal solution of sugar. During the past year our efforts have been directed almost exclusively to the construction of satisfactory cells, and not to the careful measurement of osmotic pressures, the former problem being obviously the really serious obstacle in the way of the direct measurement of this force.

The problem has not yet been solved to our entire satisfaction, but considerable progress has been made, and we propose to describe some of the difficulties which we have experienced in the course of our work and the means which we have employed to overcome them.

Porous cups, such as are used for other purposes, were found unsuitable for the construction of osmotic cells in which high pressures were to be developed, and we were compelled to enlist the aid of the potters in order to obtain cups which should meet our requirements. The ordinary porous cup is too soft, and, therefore, too weak, and is usually made of too coarse material. Its walls are also likely to contain cavities of such size as to interfere with the best results in membrane formation. Our experience has shown us that the best effects are produced in cups made of rather fine materials, very uniformly mixed, and hard burned. A high degree of porosity is not essential, while the hard burning of the cups greatly increases their strength. That great strength is necessary will be understood when we state that the total pressure attained in some of our cells amounted to over 3,000 kilograms. The bursting of the cups before the maximum pressure was reached has not been an unusual occurrence.

We have had made for us, in accordance with specifications which seemed likely to yield a satisfactory product, two varieties of cups which differed principally in respect to the internal dimensions and to the thickness of the walls. One of these has a depth of 75 mm., an internal diameter at the top of about 22 mm., and at the bottom of 18 mm. The thickness of the wall is about 4 mm. At the top of the cup there is a rim with a thickness equal to that of the wall and a depth of

8 mm. The other variety of cup has a depth of 80 mm., an internal diameter at the top of 25 mm., a wall twice as thick as the first, and a thicker and wider rim.

One of the cups of the thinner-walled variety remained unbroken at a pressure exceeding 30 atmospheres, while others have cracked under a pressure as low as 17 atmospheres. Our experiments thus far have been mainly with the thinner cups, and we are unable to state what pressures the thicker ones may be expected to stand.

The accompanying figure (Fig. I.) represents the earlier form of our apparatus. It consists of the porous cup *A*, the glass tube *B*, and the closed manometer *C*. The lower end of the glass tube is provided with a narrow rubber ring, *a*, of such thickness as to fill very tightly the space between the glass and the wall of the cup. In order to give the cement (litharge and glycerine) which is used to fill the space above the rubber ring a more secure hold upon the wall, one or more channels are cut in the wall by slowly turning the cup around a rapidly revolving carborundum or emery disk. The upper exposed surface of the cement is painted with a solution of rubber, or of rubber and paraffin, in carbon bisulphide. The upper end of the glass tube is considerably contracted by softening the glass in the flame, the purpose being to give the rubber stopper carrying the manometer greater security in its place, and to crowd the rubber toward the manometer tube and thus diminish the danger of leakage between it and the latter. A short distance below the upper end of the tube the
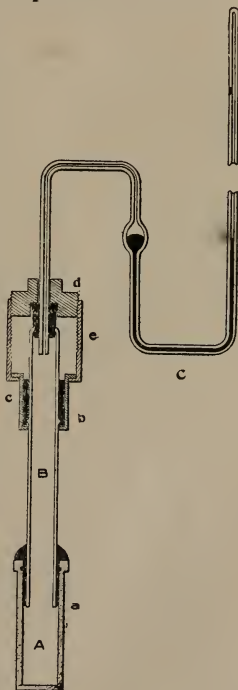
Fig. I.

ring *b* is made.   The brass piece *c* is fastened in its place with
the usual litharge-glycerine cement.   The nut *d*, through
which the manometer passes before entering the rubber stop-
per, is threaded to fit the collar *e*.   By turning *e* while the nut
is held, the stopper may be crowded into the tube and any de-
sired initial pressure produced within the cell.   The manom-
eter tube has a base of about 1 mm.   The length of the grad-
uated portion is from 30 to 70 cm., which is carefully
calibrated by means of mercury threads before closing the tube
at the top.   The volume of the calibrated space is also deter-
mined by weighing the mercury which fills it.   To prepare
the manometer for use, it is attached by means of a rubber
tube to another glass tube of the same kind as the manometer
itself, and filled with mercury.   Air, which has been freed
from carbon dioxide by means of potassium hydroxide, and
which has been dried over resublimed phosphorus pentoxide,
is then drawn into the manometer after the receding mercury
until the calibrated portion of the tube has been filled at at-
mospheric pressure.   The manometer is then closed by fusing
the glass at the upper end.   In order to avoid a possible con-
tamination of the air in the manometer with carbon dioxide,
the central portion of a large platinum disk is heated by the
blowpipe to a high temperature, and having slightly dimin-
ished the pressure on the gas within, the end of the manome-
ter, as soon as it is detached from the supply of dried air, is
passed quickly over the heated spot on the side of the disk
opposite to the blowpipe.   In this way the tube is almost in-
stantly closed, and the only possible contamination of the air
is a trace of water vapor.   The pressure within the manome-
ter is then still further reduced and the glass at the end thick-
ened by softening it in a small flame.

The closing of the manometer in this way introduces, of
course, some uncertainty as to the exact volume of the upper
end, which sometimes has a spherical and sometimes a conical
shape, and it will be necessary, when exact measurements of
osmotic pressure are attempted, to cut off and recalibrate the
upper end of the manometer after the work of measuring has
been completed.   This will be especially necessary when high

pressures are to be measured—when, for example, as in some of the cases which we shall mention hereafter, a rise of 1 mm. in the mercury amounts to nearly a whole atmosphere of pressure. For purposes of exact measurement, however, it will probably be advisable to use much longer manometers. Having filled the manometer, the air in it is brought to atmospheric pressure by raising or lowering the attached tube, its volume and temperature are ascertained, and its volume under standard conditions calculated.

The method which was employed earlier to remove the air from the walls of the porous cup has been found to work very satisfactorily. As formerly, the cell, when finished, is filled with a 0.05 per cent solution of potassium sulphate and surrounded by the same liquid. A current is passed from an electrode outside of the cell to one within, the voltage being raised until an "endosmose" in the inward direction is obtained which amounts to about 500 cc. per hour. After about a liter of liquid has been forced through the walls in this manner, the solution of sulphate is replaced by distilled water and the current again passed for some time. This procedure is repeated until the liquid almost ceases to conduct the current. The cell is then immersed and allowed to stand in recently boiled distilled water until required for the formation of the membrane. To prepare the latter, the emptied cell is placed in a beaker glass. A long platinum rod, which is to serve as cathode, is lowered into the cell. As anode, a cylinder of copper is used. There is also inserted in the cell a siphon, which reaches very nearly to the bottom of the cup and is closed at the outer end with a piece of rubber tubing and a pinch-cock. The purpose of the siphon is to remove the liquid from the cell from time to time in order to prevent an accumulation of alkali, which is believed to affect the membrane injuriously if present in more than minute quantities. When all is in readiness and the circuit closed, the potassium ferrocyanide (N/10) and the copper sulphate solution (N/5) are introduced simultaneously, the former into the cell and the latter into the beaker containing the anode and the cell. In the beginning, owing to the fact that the porous walls are

filled with nearly pure water, there is very little current.
The current, however, within a minute or two begins to in-
crease. Then, within a very short interval, it begins to fall,
and continues thereafter to decrease steadily until the maxi-
mum resistance of the cell is reached. This varies greatly.
Ordinarily it is above 10,000 ohms, often double this amount,
and in one case it exceeded 200,000 ohms. We are not yet
satisfied that this variation in the maximum resistance of the
different cells is dependent exclusively upon the membranes
themselves. We have had reason, on some occasions, to sus-
pect that a failure to reach very high resistances was due to
defects in the construction of the cell or to the character of
the porous wall, and not to the resisting power of the mem-
brane. The formation of a membrane, that is, the time re-
quired to reach the highest resistance, usually occupies from
one to two hours. We cannot yet give any definite opinion
as to the electromotive force which it is most advantageous to
employ. We use in our work a one horse-power motor-gen-
erator, which transforms a 110-volt battery current to 250
volts. We have in series with the field of the dynamos a
rheostat of so wide a range that we are able to depress the
voltage by small intervals from its maximum, *i. e.*, 250 to 30
volts. We are under the impression, however, that the lower
voltages are not advantageous and have ordinarily employed
an electromotive force ranging from 110 to 150 volts. We are,
furthermore, under the impression that when a perfect cell
has been constructed an even higher voltage will be found to
be desirable. We have, of course, made a great many obser-
vations in connection with the amount of electromotive force
employed in forming the membranes, but they have little value
because the principal difficulties which we have had to meet
have not had their cause in defects of the membrane, but were
due rather to other features in the construction of the cell.
In other words, we have not been able to connect, in cases of
failure to obtain satisfactory results, the cause of the failure
with the voltage which had been employed in making the
membrane. During the formation of the membrane it has
been our practice to withdraw the solution of ferrocyanide

from the cell and to replace it with a fresh one once every three or four minutes, somewhat oftener during the earlier than in the later stages. If the alkali is allowed to accumulate in the cell, the membrane, or parts of it, sometimes acquires a dark-brown color, apparently due to the formation of copper oxide. It was stated in the earlier communication that the membrane is located within the wall about equidistant from the two sides. This has been found to be true only of comparatively soft cups. In the hard-burned ones, which we are now using, the membrane is always deposited upon the interior surface of the cup and extends into the wall only where there are minute cavities, and in these it is continuous from the interior surface to the end of the cavity, so that one often sees, after breaking a cup, brown streaks on the fracture-surfaces, extending in some cases half way through the wall. Having completed the formation of the membrane, the cell is emptied, several times rinsed within and without with distilled water, and then, if not immediately required, it is placed in distilled water, filled with the same, and allowed to stand until needed for use.

We have used thus far, for the purpose of testing our cells, only half-normal and normal solutions of sugar. To these we have added a small quantity of potassium ferrocyanide, usually just enough to make the solution $N/100$ or $N/1000$ with respect to the salt. To the distilled water, with which the cells were surrounded, there has been added a chemically equivalent quantity of copper sulphate. That is, if the sugar solution within the cell was $N/100$ with respect to potassium ferrocyanide, the water without was made $N/100$ with respect to copper sulphate. And if the sugar solution was $N/1000$ with respect to the first salt, the water without was made $N/1000$ with respect to the second. Such solutions are, of course, not exactly equivalent osmotically, there being a slight advantage in favor of the sugar solution, owing to the fact that the potassium ferrocyanide molecule dissociates into five ions, while 2 molecules of copper sulphate yield only four, and also to the fact that the former salt is somewhat more highly dissociated than the latter. The use of the ferrocyanide and of the sul-

phate in this way is of assistance in the detection of breaks and other leaks in the cell.

The capacity of the cells made with the thinner cups has varied from 50 to 70 cc., according to the diameter and length of the glass tube. Before filling, they are rinsed a number of times with small quantities of the sugar solution which is to be used. To provide for the overflow which must occur when the stopper is inserted, we have employed a little implement made from an ordinary round file. On one side of the untempered end of the file a channel is cut. The end is then bent to a hook shape, filed down and smoothed to avoid scratching the glass. This is inserted with the stopper and allowed to remain until the latter has been crowded into the glass tube as far as it can be made to go by the hands. It is then withdrawn, the brass nut is lowered upon the stopper, and the metal collar screwed up until the nut begins to exert a slight additional pressure upon the stopper, which is indicated by the rise of the mercury in the manometer. At this point the cell is placed in water and fixed in its position. The nut is then held by means of a wrench, while the collar is turned in order to drive the stopper somewhat further into the glass tube. Ordinarily, we have forced the stopper down in this manner until the manometer indicated a pressure of from one to two atmospheres.

After closing the cell and screwing up the brass collar, the mercury in the manometer usually begins to rise within a few minutes and continues to do so until the maximum pressure is reached or until some defect in the cell is developed. The rise is frequently very rapid at first, corresponding in some cases of normal solutions to an increase of pressure of 10 or more atmospheres (and in one instance over 20 atmospheres) within an hour. At other times the rise of the mercury is slow, but in such instances the cells usually develop defects at comparatively low pressures, and apparently the slow increase of the pressure is due not so much to the difference in the activity of the membranes of individual cells as to the fact that the defects operate from the beginning, but not for some time in a sufficient degree to counterbalance the increase of pressure.

We have not made any systematic observations on the rate at which pressures develop, because data of this kind are of little value as long as the evolution of the cell is incomplete, that is, until a cell has been produced which will surely stand, without failures of any kind, the maximum pressures of the solutions for which it is intended. It can, however, be said in general, as would be expected, that the rate at which the pressure in the cell increases constantly diminishes.

It has been predicted that a serious obstacle in the way of the direct measurement of osmotic pressure would be found in the long time which would probably be required for the development of the maximum pressures of solutions. But we have discovered no reason so far for thinking that this fear will be realized. We are not able to affirm that we have obtained the maximum pressures of either normal or half-normal solutions, but we have probably very nearly reached the limits for both of these concentrations, and the time occupied in doing so has not, in any case, been very long.

The cell in its original form developed a number of serious defects :

1. The glass tube, on one occasion when the pressure in the cell exceeded 26 atmospheres, was pushed upward through the cement with which it was fastened in the cup. This difficulty was easily remedied by slightly enlarging the tube just above the rubber band.

2. The glass tube, notwithstanding careful annealing, frequently broke at or near the ring at the upper end. This difficulty was remedied in the same manner as the first by replacing the ring with a small bulb blown in the tube.

3. The liquid was often forced out of the cell between the rubber stopper and the manometer tube. This has been one of the most persistent of our troubles and it has not yet been fully mastered. We have greatly diminished, and sometimes entirely removed, the difficulty by placing between the stopper and the nut, through which the manometer passes, a brass ring which had been hollowed out to a conical form upon the under side, and by tightly winding the upper end of the stopper with narrow strips of insulating tape. The effect of

this arrangement is to crowd the upper end of the stopper more and more tightly against the manometer as the stopper is forced downward by the nut above. Another device designed to produce the same effect will be described later. On four occasions the manometer itself has been pushed upward out of the rubber stopper. The cause of this is, of course, the same, namely, the failure to crowd the rubber sufficiently hard against the manometer tube.

4. It was found, in several instances, that the cement employed to fasten the glass tube into the cup had been somewhat disintegrated by the action of the liquids which penetrated the wall of the cup from the outside and came into contact with it. And the failure of a number of our cells to develop more than very moderate pressures is to be ascribed to this cause. The measures adopted to overcome this difficulty will be better explained when we come to describe the most recent form of our cell. It is sufficient to say here that we now line the cavity occupied by the cement with a coating of rubber, which is afterwards hardened or vulcanized. By this process, together with the painting of the upper exposed surfaces of the cement with rubber, we prevent any contact whatever of the cement with liquids.

5. We have stated that the rubber band at the bottom of the glass tube was crowded very tightly against the wall of the cup, and especial pains has been taken to give the lower edge of the rubber as much support as possible in this way. Nevertheless, our cells have failed more frequently in consequence of a slight movement under pressure of the lower edge of this band than from any other one cause. The upper limit of the membrane is at the lower edge of the rubber band, and if the rubber is pushed upward or sidewise in the slightest degree, as it often has been, a portion of the wall not covered by the membrane is exposed and a leakage into the wall is the result. It was mainly for the purpose of detecting a leak of this kind that we have been accustomed to add a little potassium ferrocyanide to the sugar solution and a little copper sulphate to the water in which the cell was immersed. It should also be said that at times there has been a leakage of

the sugar solution between the rubber band and the glass tube into the cement. The failure of the rubber band to remain rigid can be detected when the leakage is into the wall of the cup by the peculiar movements of the mercury column in the manometer. The mercury rises continuously, and perhaps rapidly, until a pressure of several atmospheres is indicated, then suddenly it falls perhaps 2 or 3 mm., then begins to rise again, going the second time higher than before, at times very considerably higher. It then falls again as before, only to be succeeded by another and higher rise of the mercury. This conduct is clearly due to the formation of new membranes over the surface exposed in consequence of the crowding up or aside of the lower edge of the rubber band. When a leakage at the stopper occurs, the movements of the mercury column are usually somewhat different from those just described. The first effect of the leakage is ordinarily a marked diminution in the rate at which the mercury rises. This slackening becomes more and more pronounced until at a certain point the column suddenly falls a few millimeters. It then rises about to the point it first reached and falls again as before. Usually this behavior continues until the cell is taken apart. In such cases it is evident that the liquid is forced out from time to time in small portions and only as a certain definite pressure is reached. The process may continue until the contents of the cell have become considerably diluted, but as the dilution proceeds the time required for the mercury, after a fall, to reach its previous elevation naturally increases. Sometimes, however, when a leak at the stopper occurs, the mercury rises rapidly at first, then much more slowly, but continuously, until its highest point is reached, where it remains perhaps for days, if the leak is a minute one, without sensible movement in either direction. The meaning of this conduct is, of course, that the leak is continuous and not intermittent as in the first case. Frequently, when a cell gave indications of a movement of the rubber band, we have taken it apart, washed it, and then subjected it to the same treatment as when the membrane was first formed, that is, we have attempted to deposit electrolytically

a membrane over the places exposed in consequence of the movement of the rubber band. Occasionally this treatment has been repeated as many as three times with the same cell, and usually the process has been satisfactory to this extent, that we were able, after such a course, to obtain considerably higher pressures than at first. But not any of the cells which proved themselves defective in respect to the rubber band have ever given us what we suppose to be the maximum pressures of the solution.

In the new form of cell (Fig. II.), we have substituted a porcelain tube for the glass one. We were led to do so by certain unpleasant experiences with the material from which our glass tubes were made. All the cells made during a period of several weeks were lost in consequence of the cracking of the glass tubes, often in the most unexpected places and apparently without cause. The real explanation is probably that the glass, which had been in the laboratory for some years, had suffered deterioration. Another reason for making use of porcelain instead of glass was that the portion occupied by the rubber stopper could be ground into a form which seemed likely to diminish the difficulty which we have always had in keeping the stopper and the manometer in their places. The porcelain tubes which were available for our purposes were un-
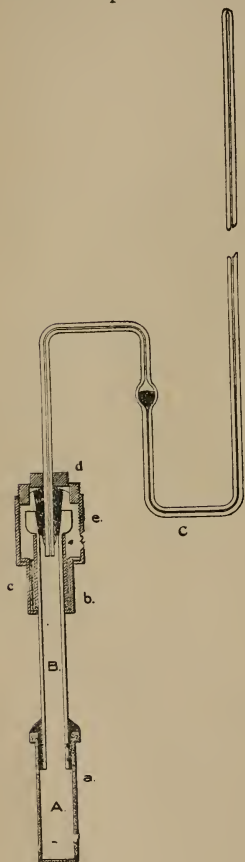
Fig. II.

glazed ones and we feared, notwithstanding the fact that they had evidently been heated to very high temperatures, that they would develop leaks under high pressures. To test them with respect to their possible porosity, we plugged one end and soaked them over night in a salt solution, and then tested the walls as to their conductivity between the poles of our dynamo while developing 250 volts. No current could be detected. In order to make use of the porcelain tubes according to our new plan for the cell, it was necessary to grind a portion of one end—the one located in the cup — perfectly round externally, and at the other end to grind a "seat" for the rubber stopper, which should have a taper somewhat greater than the stopper itself. The proper centering of the tube for grinding of this kind cannot be accomplished by any of the usual tools of the mechanic. We therefore made for ourselves the "chuck" which is represented in Fig. III. *A* is a steel tube having a length of 12.5 cm., and a hole 2.5 cm. in diameter from end to end. Near each end are three machine screws symmetrically located around the tube. The porcelain tube, which is to be shaped, is fastened between the ends of the two sets of three screws each. This arrangement permits

Fig. III.

any desired adjustment of either end of the tube. Around the central portion of the steel tube *A* is an accurately fitted steel ring, *B*, which is provided with oil holes. At each end of the ring there is a collar, *C*, with a set screw. As all parts of the tool are perfectly fitted, the tube *A* turns in its collar easily and accurately. The ring itself is made stationary between
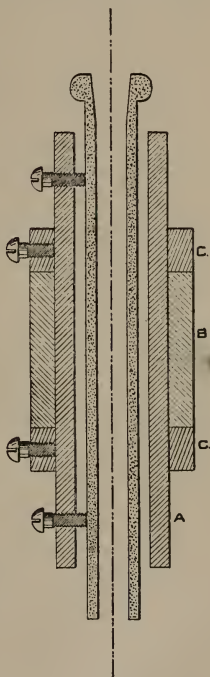
the jaws of the "back-rest" of the lathe. The porcelain tube, after adjustment, may be turned during the grinding by the hand, or by a pulley and belt, or the tube may be joined to the "live" spindle of the lathe. The grinding is done by means of carborundum or emery disks fastened upon the ends of small steel mandrels which are held in the chuck of a "traveling" grinder, the grinder being attached to the tool-carriage of the lathe. This being compound, the grinding disk may be made to move back and forth at any angle to the axis of the porcelain tube. The grinder which we use has a speed which may be varied between 2,000 and 5,000 revolutions per minute. At these rates the porcelain can be quickly shaped without danger of impairing the strength of the tube, since the grinding disk may be made to touch the porcelain so lightly that there is practically no jarring of the tube.

As stated already, the seat for the stopper is given a somewhat greater taper than that of the stopper itself. The result of this form is that, as the stopper is pressed forward into the tube, it is crowded more and more tightly against the manometer tube. Another device which has been of great assistance to us in securing the manometer in the rubber stopper may be mentioned here. The end of the manometer tube is made to project 2.5 or 3 cm. beyond the lower end of the stopper and is heated to a temperature somewhat above the fusing-point of shellac, and while hot, covered with the gum in order to secure good adherence to the glass. Afterwards portions of molten shellac are deposited upon the tube near the stopper and allowed to solidify until a considerable quantity has accumulated. The tube is then held vertically and the shellac cautiously and uniformly heated, but not so high as to produce a thin fluid condition. In this state it gradually descends and solidifies, forming upon the tube a conical enlargement. Now if the tube is forced upwards under the pressure in the cell, the apex of the cone enters the stopper, spreading the rubber sidewise, tightening both stopper and manometer in their places.

In order to give the cement a more secure hold upon the

porcelain tube, there are cut into the tube in that portion covered by the former, a number of horizontal gashes or furrows, a grinding-disk with a wedge-shaped edge being employed for the purpose.

The arrangement for securing the stopper is necessarily somewhat more complicated than when a glass tube is used. A short brass tube, somewhat smaller than the enlarged upper end of the porcelain one, is placed over the latter, and with its edge lying against the shoulder, is filled with cement. The lower edge of this brass tube serves the same purpose as the bulb at the upper end of the glass tube in the earlier form of the cell, that is, it rests upon the flange of the brass piece on which the threaded collar turns.

The substitution of a rigid ring of hard rubber or of soapstone for the rubber band, which was first used at the bottom of the tube, and which has given us so much trouble, made it necessary to grind the inner wall of the cup quite accurately as far as the lower edge of the ring. This gives us a shoulder in the cup on which the ring rests.

In order to center the cup in the lathe for the purpose of grinding the inner wall, we have employed the chuck represented in Fig. IV. It consists of the master-chuck A, which is screwed on to the mandrel of the lathe and the brass tube B, which is screwed into the master-chuck. The inside of B is threaded from end to end, and in it there are the two smaller threaded tubes C and C'. At one end of C and C' there is a flange, against which rest the soapstone rings D and D'. These rings are bored to a taper equal to that of the outside of the cups. The largest diameter of the hole in the forward ring is slightly less than that of the cup under the rim, while the largest diameter of the rear one is equal to that of the cup about one-third of the way from the bottom. With this arrangement it is practicable to center the cup quite satisfactorily and to hold it sufficiently firmly in its place during the process of grinding. The grinding is accomplished by means of carborundum disks held in the chuck of the traveling grinder already referred to.

The rings are turned to fit the ground end of the porcelain
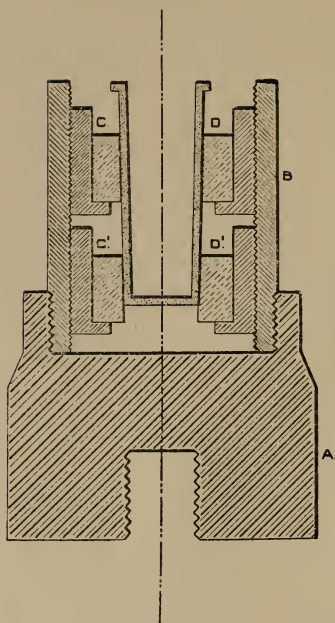
Fig. IV.

tube and the inner wall of the cup with the greatest possible
exactness.

After grinding the porcelain tube and the cup and turning
the ring, the ring is fixed in its position upon the ground end
of the porcelain tube and firmly against the shoulder above.
The tube is then inverted and the ring soldered to it with
shellac, the shellac being maintained in the molten condition
for some time in order that it may work its way inward be-
tween the two. The lower end is then painted two or three
times with a solution of rubber in carbon bisulphide, and the
rubber is afterwards hardened by maintaining it for several
hours at a temperature of from 90° to 100°.

The ring with the tube firmly attached in the manner described is placed in position on the shoulder within the cup. The cup wall above the ring is then repeatedly painted with the rubber solution. A quantity of shellac is placed upon the ring and the temperature of the cup raised until the gum fuses. It is kept in the molten condition for some time to insure its working its way between the outer edge of the ring and the wall of the cup. The cup is then placed in a hot air-bath and kept at a temperature of from 90° to 100° for several hours, or until the rubber on the wall is no longer sticky. Finally the space above the ring is filled with the cement. It is to be noted with regard to the latter that the hardening process is much more rapid if a little water is added to the glycerine with which the litharge is mixed.

Our observations on the osmotic pressures of half-normal and normal solutions of sugar have thus far been made with reference to the testing of the construction of our cells and the efficiency of the membranes prepared by the electrolytic process, and not with a view to an accurate determination of the pressures of such solutions. Nevertheless, we have accumulated some data which enable one to predict approximately what the pressure of a half-normal solution will be found to be, and to state that the pressure of a normal solution will be found to be above a certain definite value. We give below a brief record of the greater portion of the cells which were made after we had remedied the difficulties which resulted from the use of a flexible rubber ring at the bottom of the glass tube, and those which were occasioned by permitting the solutions, during the electrolysis, to soak through the cup wall where they could come in contact with the cement. It should be stated, with reference to these records, that the atmospheric pressure, *i. e.*, that upon the water outside of the cell, is, in every case, deducted from the pressure upon the air within the manometer; also that the volumes of the air within the manometer are reduced to 0° for all observations, so that the pressures recorded are simply osmotic pressures at the temperatures of the cells when the readings were made. These readings were obtained with the aid of a

standard meter and a cathetometer of the best construction, the telescope of which is provided with a micrometer eye-piece, supposed to enable one to read with a fair degree of accuracy to within $\frac{1}{500}$ mm. The values given are to some extent inaccurate in consequence of the uncertainty as to the exact form of the upper end of the manometer. As previously stated, when the manometer was closed by fusing the glass, the form of the upper end of the air space was sometimes spherical and sometimes conical in appearance, and we have assumed in our calculations that it was either perfectly spherical or conical according to the form which it resembled more closely. The error resulting from this uncertainty does not; however, exceed in any case 0.2 atmosphere and in most cases is much less than this. When we undertake to determine with accuracy the pressures of solutions, we shall, of course, after having made our measurements, open the manometers and recalibrate the upper ends.

Observations on the Osmotic Pressure of Half-Normal Solutions.

1. Resistance of the membrane, 16,307 ohms. The pressure rose in twenty-five hours to 11.34 atmospheres at 23°.1, when the manometer was pushed out of the cell.

2. Same cell as No. 1. Resistance of the membrane, 16,307 ohms. The pressure rose in twenty-two and a half hours to 13.2 atmospheres at 24°.3, when the manometer was accidentally broken.

3. Resistance of the membrane, 108,000 ohms. Filled with a sugar solution which had been made ten days before. The pressure rose in twenty-five hours and fifteen minutes to 14.51 atmospheres at 22°.8. Cell taken down and solution examined with Fehling's solution. The sugar was found to be somewhat inverted.

4. Resistance of the membrane 110,000 ohms. Filled with a fresh solution of sugar which did not reduce Fehling's reagent. The pressure rose slowly in ninety-five hours and twenty-six minutes to 12.78 atmospheres at 25°.6. The cell is believed to have leaked at some point, but the defect could

not be located with certainty. The solution, after removal from the cell, reduced Fehling's solution very slightly.

5. Resistance of the membrane, 12,111 ohms. Filled with a fresh solution of sugar. The pressure rose to 11.83 atmospheres in forty-seven hours. The cell was found to be leaking and was taken down.

6. Resistance of the membrane, 14,625 ohms. Solution of sugar not freshly made. The pressure rose to 13.52 atmospheres at 23°.4 in fifty-two hours and forty minutes, when the manometer was forced out of the cell.

7. Resistance of the membrane, 29,000 ohms. Filled with a fresh solution of sugar. The pressure rose in two hours and fifty minutes to 8.94 atmospheres; in the following three hours and fifty minutes to 12.33 atmospheres; in the succeeding four hours and forty minutes to 13.39 atmospheres; and then in the next eighteen hours, to 13.58 atmospheres at 20°.5. The pressure remained constant for thirty hours longer, when the cell was taken down. The solution was not examined for inversion.

8. Resistance of the membrane, 110,000 ohms. Filled with a fresh solution of sugar. The pressure rose in one hour and forty minutes to 7.72 atmospheres; in the following seventeen hours and thirty minutes, to 10.56 atmospheres; in the succeeding ten hours and forty-five minutes, to 13.10 atmospheres; then in thirty-three hours and forty-five minutes, to 14.03 atmospheres. The pressure then remained practically constant for seventy-two hours, the last reading being 14.08 atmospheres at 25°.2 when the cell was taken down. The solution from the cell was accidentally lost, and therefore not examined for the inversion which our experience with other cells leads us to believe had occurred to some extent.

Observations on the Osmotic Pressure of Normal Solutions.

1. Resistance of the membrane, 3,303 ohms. The pressure rose in fifteen hours to 16.62 atmospheres, when the porous cup burst.

2. Resistance of the membrane, 6,316 ohms. The pressure rose in forty-one hours to 16.61 atmospheres, when the cell was found to be leaking at the stopper.

3. Same cell as in No. 2, but resubjected to the membrane-forming process. Resistance, 2,698 ohms. The pressure rose in sixty-nine hours to 22.02 atmospheres at 22°.3. The manometer was displaced by the pressure and the cell was found to be leaking at the stopper.

4. Resistance of the membrane, 16,000 ohms. The pressure rose to 19.6 atmospheres in six hours, when the manometer was pushed out of the stopper.

5. Resistance of the membrane, 21,000 ohms. The pressure rose in three hours and twenty-five minutes to 19.32 atmospheres, and in the succeeding twelve hours to 22.88 atmospheres. The cell was then found to be leaking. It was opened, but as there appeared to be no escape of liquid around the stopper it was closed again without change of contents. In ten hours the pressure rose to 22.01 atmospheres, when it began to fall and the cell was taken down.

6. Resistance of the membrane, 7,648 ohms. The pressure rose in seven hours and 42 minutes to 21.98 atmospheres, when the porous cup burst.

7. Resistance of the membrane, 6,750 ohms. The pressure rose in five hours and forty-five minutes to 19.3 atmospheres. Cell found to be leaking at the stopper. It was refilled, and in four hours and thirty minutes the pressure rose to 18.68 atmospheres. As the pressure would rise no higher the cell was taken down for investigation.

8. Resistance of the membrane, 6,000 ohms. The pressure rose in seventeen hours and forty-five minutes to 21.42 atmospheres. The cell was found to be leaking around the manometer tube. It was refilled, and in five hours and thirty minutes the pressure rose to 26.96 atmospheres at 21°. During the five succeeding days there was no noticeable change of pressure, but at the close of this period the cement gave way and the glass tube was pushed out of the cell. The sugar solution used in this experiment was freshly made and free from invert sugar. It was made only N/1000 with respect to potassium ferrocyanide.

9. Resistance of the membrane, 12,033 ohms. Solution N/100 with respect to potassium ferrocyanide. The following are the data concerning the pressures developed :

Pressure at 12 M., 17.31 atmospheres.
     "   1 P.M., 21.72   "
     "   3.15 "   26.04   "
     "   4.00 "   26.74   "
     "   5.00 "   27.51   "
     "   5.25 "   28.11   "

At 5.40 P.M. the porcelain tube burst. The last reading corrected for temperature gave a pressure of 27.63 atmospheres at 19°.6.

10. Resistance of the membrane, 54,000 ohms. Cell set up at 5.40 P.M. The following readings were obtained :

Pressure at 5.55 P.M., 12.43 atmospheres.
     "   6.20 "   19.65   "
     "   6.40 "   20.83   "
     "   6.50 "   21.68   "

At 7.00 P.M. the glass tube was shattered.

11. Resistance of the membrane not exactly known, but over 200,000 ohms. Solution of sugar N/100 with respect to potassium ferrocyanide, and the water in which the cell was immersed N/100 with respect to copper sulphate. The solution of sugar fresh and free from invert sugar. Cell set up at 5 P.M. Pressure at 5.10 P.M., 7.89 atmospheres ; at 6.45 P.M., 31.41 atmospheres (corrected). Temperature 24°.9. Shortly after the second reading the glass tube was shattered.

It is probable that all of the solutions which remained in the cells more than twenty-four hours were slightly inverted, but whether the reaction had proceeded in any case to an extent which materially affected the osmotic pressure of the solution is not known. This is a matter which must be carefully investigated when accurate measurements are attempted. Our sugar solutions were prepared from the purest obtainable '' rock candy,'' and when first made up, they did not reduce Fehling's solution.

We conclude from the results recorded above that the osmotic pressure of a half-normal solution will be found to lie between 13 and 14 atmospheres at temperatures in the neighborhood of 20°, and probably between 13.4 and 13.8 atmospheres. And it is certain from the last experiment with normal solutions (No. 11) that the pressure of a normal solution

of sugar is not less than 31.4 atmospheres. The solution in this case was fresh and free from invert sugar, and the highest pressure was reached within two hours after the solution had been made. During so short an interval no appreciable inversion could have occurred. In other words, the whole observed pressure was undoubtedly due to molecules of cane sugar.

The divergence of the pressure of a half-normal solution (if it is found to be between 13° and 14 atmospheres) from the theoretical value is interesting in connection with the abnormal freezing-point of a sugar solution of the same concentration. If the osmotic pressure of a half-normal solution of sugar deviates in the same degree from the theoretical as does the freezing-point, the pressure should be about 13.5 atmospheres.[1] A similar divergence from the theoretical value on the part of a normal solution of sugar would give for it an osmotic pressure of about 33 atmospheres, that is, about 1.5 atmospheres above the pressure reached in our last experiment, in which the pressure had pretty certainly not reached its maximum when the cell was shattered.

The evolution of the cell has now reached the point where we think it admissible for us to undertake a more careful determination of osmotic pressure, and we shall, in the immediate future, attempt to ascertain with a much greater degree of exactness the pressure of half-normal and normal solutions. The measurement of the pressures of solutions of intermediate and lower concentrations will be undertaken by others working in this laboratory. We shall also attempt to make membranes by the electrolytic process from other substances than copper salts and ferrocyanides, and to ascertain how far electrolytically prepared membranes may be utilized for the study of the dissociation of electrolytes. In the meantime we shall endeavor to improve the cell. Very much remains to be learned with regard to the conditions which are favorable or unfavorable to the production of a perfect membrane. So far as we know, we have produced the ideal membrane in one instance only; namely, in the case of the last experiment, when the membrane almost ceased to permit the passage of the cur-

[1] Jones: Ztschr. phys. Chem., **12**, 642.

rent and exhibited such astonishing efficiency that the pressure rose to over 31 atmospheres in less than two hours. It is possible, however, that we have had equally good membranes on other occasions and that their failure to work as well was due to faults not inherent in the membranes themselves. It is of the utmost importance to ascertain the conditions under which such a membrane as our last one can be produced at will.

The difficulties of construction are by no means completely overcome, and we have in view a number of changes which we hope will prove of advantage. That these difficulties are of great magnitude will be realized if one considers that in our last experiment the pressure which was measured and which was still below what we were called upon to control would suffice to raise a column of water at 20° to a point 15 meters higher than the top of the Eiffel tower, or which would raise from its base a marble shaft whose height is 120 meters. These comparisons will perhaps make it clear that the most painstaking attention to every detail of construction is absolutely essential to success when an apparatus like ours is to be made up of several parts, consisting of different materials, and which must be united without the usual mechanical means of securing strong joints.

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JOHNS HOPKINS UNIV.,
June, 1902.

A REDETERMINATION OF THE ATOMIC WEIGHT OF LANTHANUM.

By HARRY C. JONES.

A number of determinations of the atomic weight of lanthanum have already been made. The more important and reliable are the following :

Rammelsberg[1] precipitated the sulphuric acid in lanthanum sulphate as barium sulphate. He found the atomic weight of lanthanum, from one determination, to be 133.4.

In the same year Choubine[2] published determinations of the atomic weight of lanthanum. He transformed the oxide into

[1] Pogg. Ann., **55**, 66 (1842).
[2] J. prakt. Chem., **26**, 443 (1842).

lanthanous chloride and then precipitated the chlorine by means of silver nitrate. The two determinations gave values lower than that found by Rammelsberg, but Choubine's material was almost certainly contaminated with other substances.

The same criticism applies to the work of Hermann,[1] who, the following year, made a few determinations of the atomic weight of lanthanum.

The first determination of the atomic weight of lanthanum upon which much stress can be laid is that of Marignac.[2] He titrated solutions of lanthanum sulphate with a solution of barium chloride. As a mean of nine determinations he found the atomic weight of lanthanum to be 140.2.

Holzmann[3] attempted to determine the atomic weight of lanthanum by several methods. He analyzed the sulphate by precipitating the lanthanum as oxalate, igniting the oxalate, and weighing the oxide. From three determinations he obtained for the atomic weight of lanthanum the value 138.8. He also analyzed the iodate of lanthanum by precipitating the lanthanum as oxalate and determining the iodic acid volumetrically. The lower values found by this method cannot be regarded as important, since the method has been shown to be defective. Holzmann also determined the atomic weight of lanthanum by analyzing the double nitrate of lanthanum and magnesium $(2La(NO_3)_3.3Mg(NO_3)_2.24H_2O)$. This method, like that involving the use of the iodate, is open to serious objection.

In 1860 Czudnowicz[4] published one analysis of lanthanum sulphate, and a year later Hermann[5] analyzed both the sulphate and carbonate of lanthanum. Since the material was not purified with sufficient care, no stress can be laid upon the results obtained.

In 1868 Zschiesche[6] freed his lanthanum from didymium and made six analyses of lanthanum sulphate. The values

[1] J. prakt. Chem., **30**, 199 (1843).

[2] Arch. Sci. Phys. et Nat., [1], **11**, 29 (1849).

[3] J. prakt. Chem., **75**, 343 (1858).

[4] *Ibid.*, **80**, 33 (1860).

[5] *Ibid.*, **82**, 395 (1861).

[6] *Ibid.*, **104**, 176 (1868).

found for the atomic weight of lanthanum differ more than three units. The mean value is 135.9.

Erk[1] analyzed the sulphate of lanthanum by precipitating the lanthanum with ammonium oxalate, igniting the oxalate and weighing the oxide. The mean of three determinations gave for the atomic weight of lanthanum the value 135.5.

Erk also determined the sulphuric acid in the filtrates and from these results calculated the atomic weight of lanthanum to be 135.3.

Marignac[2] redetermined the atomic weight of lanthanum by further purifying the sulphate by repeated crystallization. In two determinations the sulphate was heated to dull redness, weighed, and then heated to a white heat to convert the sulphate into oxide. In two other determinations the dried sulphate was dissolved and the solution treated with a solution of ammonium oxalate. The oxalate of lanthanum was strongly heated to convert it into the oxide, and the oxide weighed. By the first method Marignac obtained for the atomic weight of lanthanum the value 138.9; by the second method the value 138.7.

Clève[3] made five determinations of the atomic weight of lanthanum in 1874. The oxide, analyzed spectroscopically, was dissolved in nitric acid. The solution was treated with sulphuric acid, evaporated to dryness, and the residue heated to remove all excess of sulphuric acid. The amount of sulphate formed was then weighed. The mean of Clève's determinations gave, for the atomic weight of lanthanum, the value 139.3.

Brauner[4] made his first determinations of the atomic weight of lanthanum in 1882. In two syntheses of the sulphate from the oxide he obtained for the atomic weight of lanthanum the values 138.94 and 138.83, the mean being 138.88.

In a second series of determinations published in the same year, Brauner[5] obtained considerably lower values. With this material, which Brauner thinks was purer than that originally

[1] Ztschr. Chem., N. F. **7**, 106; Ztschr. anal. Chem., **10**, 509 (1871).

[2] Ann. chim. phys., [4], **30**, 68 (1873).

[3] K. Svensk. Akad. Handlingar, **2**, 7 (1874).

[4] Monatsh. Chem., **3**, 28 (1883).

[5] *Ibid.*, **3**, 493.

used, he obtained values for the atomic weight of lanthanum ranging from 138.06 to 138.45, with a mean of 138.28.

Clève[1] published his second series of determinations of the atomic weight of lanthanum in 1883. The material which Clève used was unquestionably purer than any which had been employed up to that time. He made a series of twelve determinations by converting the oxide into the sulphate. The atomic weight of lanthanum calculated by Clève on the basis of $SO_3 = 80$ varied from 138.07 to 138.35, with a mean of 138.22. Calculated on the basis of the present values for oxygen and sulphur, this becomes 138.55. Of all the determinations of the atomic weight of lanthanum thus far made, this is apparently entitled to the greatest confidence.

Bauer,[2] in 1890, made four determinations of the atomic weight of lanthanum by converting the oxide into the sulphate. The results calculated in terms of oxygen $= 16$ and sulphur $= 32.06$ range from 138.91 to 138.3.

Bettendorff[3] made four determinations of the atomic weight of lanthanum by the same method, *i. e.*, the synthesis of the sulphate from the oxide. He calculated the atomic weight of lanthanum on the basis of $O = 15.96$, $S = 31.98$, and obtained values ranging from 138.21 to 138.24. His results calculated on the present basis, of oxygen $= 16$ and sulphur $= 32.06$, give as the atomic weight of lanthanum the value 138.62.

Wolcott Gibbs[4] carried out, in 1893, an extensive investigation on the rare earths, with special reference to methods of separating and determining these substances. He analyzed the colorless nitrate of ammonium and lanthanum furnished him by Dr. Shapleigh, by precipitating the lanthanum as oxalate and igniting the oxalate. He found for the atomic mass of lanthanum the value 139.7.

Gibbs does not seem to lay much stress upon this result as a determination of the atomic weight of lanthanum, since his work was carried out rather to test certain analytical methods

[1] Bull. Soc. Chim., **39**, 151 (1883).
[2] Dissertation, Freiburg (1884).
[3] Ann. Chem. (Liebig), **256**, 168 (1890).
[4] Proc. Am. Acad., **28**, 260 (1893).

than to purify the several elements and determine their atomic weights. Gibbs states[1] that Shapleigh found values of the same order of magnitude as his own by means of the sulphate method.

The most recent determination of the atomic weight of lanthanum is that of Brauner and Pavliček.[2] The material was purified by crystallizing the double nitrate of ammonium and lanthanum. It was then fused with potassium sodium nitrate and fractionally precipitated with potassium hydroxide. Brauner determined the atomic weight of the lanthanum in the several fractions and found it to vary from 138.78 in the most positive fraction to 139.1 in the most negative. They regard the most positive fraction as representing the purest lanthanum. They, however, think that since the sulphate is hygroscopic, from 0.2 to 0.3 should be added to the value found by experiment. When this is added to 138.78 they obtained 139.0, which they regard as the true atomic weight of lanthanum.

Brauner and Pavliček conclude that the sulphate method of determining atomic weights, as ordinarily applied, is unreliable, since the sulphate always contains acid sulphate. They used the sulphate method, but determined the amount of acid sulphate present by titrating with sodium hydroxide and introducing the corresponding correction.

This conclusion, we shall show, is not based upon a sufficient study of the facts. The presence or absence of acid sulphate depends upon the temperature to which the sulphate has been heated.

It is obvious, from the above sketch of what has been done, that the question of the atomic weight of lanthanum is far from settled. Take even the more recent and trustworthy determinations, and we find a lack of concordance amounting to several units. A careful study of these investigations will show that this is probably due to the different degrees of purity of the materials employed.

[1] Proc. Am. Acad., 28, 262 (1893).
[2] Proc. Chem. Soc., 17, 63.

Material Used.

The present investigation would not have been undertaken but for the fact that an unusually pure specimen of lanthanum was placed at the writer's disposal by Dr. Waldron Shapleigh, just before his death.

I should like to take this opportunity to express my many obligations to Dr. Shapleigh, in connection with the work already done on the atomic weights of the so-called "rare earths." He isolated lanthanum, praseodymium, neodymium, thorium, and cerium on a scale never dreamed of before his time, and placed the fruit of a score of years at the disposal of those who desired to carry out purely scientific investigations, with a liberality which is rare. Scientific, as well as technical, chemistry, has suffered an irreparable loss by the death of this most genial man.

In addition to having at my disposal remarkably pure ammonium lanthanum nitrate by the kilogram, the unusual spectroscopic facilities offered by the physical department of this university, in the Rowland spectroscope, made it highly desirable that the atomic weight of lanthanum should be carefully studied.

The double nitrate of ammonium and lanthanum was subjected to fractional crystallization until spectrum analysis showed that it was homogeneous and contained as impurity only a trace of cerium. The double nitrate was heated in small quantities over the blast-lamp until only the oxide of lanthanum remained.

To remove any trace of the nitrate which might not have been decomposed, the resulting oxide was boiled for a considerable time with water which had been purified by the method described by Jones and Mackay[1] for preparing water for conductivity measurements. Indeed, all the water used in this work was purified by this method.

The oxide was filtered off and thoroughly washed with hot water. It was then treated with hot, dilute nitric acid, and dissolved, leaving, however, a slight cloudiness, which was basic cerium nitrate. The solution was then filtered repeat-

[1] This JOURNAL, **19**, 91 (1897).

edly through the same filter until it was perfectly clear.

The solution of the nitrate was then treated with a dilute solution of oxalic acid, which had been purified as follows : Commercial oxalic acid was dissolved in redistilled, cold water. The solution was concentrated by evaporation and crystals of the acid obtained. The crystals were then dissolved in a mixture of equal parts of pure, anhydrous ethyl alcohol and pure, anhydrous ether. In this way the oxalic acid was freed from every trace of metallic salts.

To the solution of the oxalic acid in alcohol and ether 3 to 4 volumes of water were added and the mixture boiled for some time, until the ethyl oxalate formed had been decomposed. The solution was then evaporated and the oxalic acid allowed to crystallize.

The oxalate of lanthanum was precipitated from the nitrate in the presence of nitric acid. In this way it was separated from all of the more common impurities, such as calcium, iron, etc.

The oxalate was then decomposed to the oxide and analyzed spectroscopically by Mr. L. E. Jewell, whose work in this field is so well known. The only impurity which could be detected was a trace of cerium, and this was not more, and probably much less, than 0.01 per cent.

The oxalate was again decomposed to the oxide, the oxide dissolved in hot, dilute nitric acid, and the lanthanum precipitated again as the oxalate. The oxalate was decomposed over the blast-lamp and the resulting oxide used for the following determination :

To determine whether the oxide prepared in this way contained any oxide richer in oxygen than the sesquioxide, a specimen was heated in an atmosphere of hydrogen. The oxide was placed in a porcelain boat and the whole weighed. The boat was shoved into a hard-glass tube and the tube heated in a combustion-furnace until the glass began to soften ; a stream of hydrogen, purified by passing through solutions of sodium plumbate and silver nitrate, and dried, being led through the tube. After the oxide had been heated to redness for about an hour it was allowed to cool in an at-

mosphere of hydrogen, and then placed in a desiccator over phosphorus pentoxide until weighed. No loss in weight could be detected. The oxide was then returned to the glass tube and reheated for a second hour in an atmosphere of hydrogen. It maintained perfectly constant weight. From these experiments the conclusion was drawn that the oxide of lanthanum prepared by decomposing the oxalate is the pure sesquioxide, free from any higher oxide.

Carrying Out a Determination.

The glaze was removed from the inside of a porcelain crucible by treating it with hydrofluoric acid, and the resulting dust brushed out with the greatest care. Indeed, the crucible was scoured with a button-brush turned in a lathe, until every particle of loose material had been removed. This was done to prevent the oxide of lanthanum from coming in contact, while hot, with the glaze on the crucible and the possible formation of a silicate of lanthanum. The glaze was not removed from the exterior of the crucible, since its presence prevented any reducing gases from the flame from passing through the porcelain and coming in contact with the oxide.

The desired amount of lanthanum oxide was placed in the porcelain crucible and heated over the blast-lamp to constant weight.

A platinum crucible was placed in a weighing tube with a ground-glass stopper and weighed. The oxide of lanthanum was quickly transferred from the porcelain crucible, in a desiccator containing phosphorus pentoxide, to the platinum crucible. The latter was quickly introduced into the weighing tube and the whole reweighed. In this way the weight of the oxide used in an experiment was determined.

The weighings were made to 0.00005 gram. The writer is of the opinion that this is sufficiently accurate for refined atomic weight determinations, since every chemist is fully aware that the most accurate operation carried out in a chemical laboratory is the weighing with a satisfactory balance. The weighings were made to 0.05 milligram, and the 0.1 milligram nearest to the value found was taken as the true

weight. The error in weighing was thus quite as small as in the remaining operations connected with the carrying out of the method.

The oxide was then treated with a measured volume of fairly concentrated sulphuric acid and warmed very gently until it had been transformed into the sulphate. Unless this precaution is taken the reaction is liable to take place with some violence and cause the substance to spatter upon the sides and top of the crucible. The sulphate was then evaporated slowly to dryness in an upright air-bath, the crucible resting upon a porcelain triangle about 2 cm. from the bottom of the bath. The sulphate was then heated sufficiently high to decompose all acid sulphates which might have been formed. It was then reheated until constant weight was established.

Proof of the Absence of Acid Sulphates.

The question of the presence of acid sulphates of lanthanum was studied with care, especially since Brauner[1] had stated that under these conditions Wyrouboff's acid sulphate was always present. Indeed, Brauner and Pavliček determined the amount of the acid sulphate present under the conditions with which they worked by titration with sodium hydroxide.

The sulphate of lanthanum which had been heated to constant weight was at first treated with a few drops of a solution of ammonium carbonate and reheated. It lost in weight very considerably and continued to do so as more and more ammonium carbonate was added. This led to the conclusion that the lanthanum sulphate was undergoing decomposition in the presence of ammonium carbonate, giving rise to lanthanum carbonate, and ammonium sulphate which was volatilized at the temperature employed. This was proved by the fact that when the lanthanum sulphate was dissolved in water a very considerable insoluble residue remained behind. Indeed, this is just what we would expect when we consider that lanthanum is such a weak base. This is the probable explanation of the fact pointed out by Brauner and Pavliček

[1] Proc. Chem. Soc., **17**, 63 ; Centrbl., 1901, 1035.

that when ammonium carbonate was added to lanthanum sulphate, which had been heated to 450°, a further loss in sulphuric acid took place.

The method of testing for the presence of acid sulphate was the following: The sulphate was heated to constant weight and dissolved in water. The solution was perfectly clear, showing that none of the sulphate had been decomposed. The solution was then tested to see whether it would show an acid or basic reaction. In every determination the solution of the sulphate was found to be perfectly neutral, showing not the slightest trace of acid or basic properties.

These facts, together with the complete solubility of the sulphate, show that we had to deal with the normal sulphate, free from both acid and basic salt.

A volume of the sulphuric acid just equal to that used in each determination was evaporated to dryness and the residue weighed. The residue was found to weigh 0.00002 gram.

The Results.

Twelve determinations were completed by the method described above, and the results are given below, calculated on the basis of oxygen $= 16$, sulphur $= 32.06$. These include every determination which was completed. A few determinations were lost by accident, especially in the earlier stages of the work, due to the spattering of the sulphate upon the lid of the crucible. These determinations were interrupted as soon as any spattering was discovered, and the resulting sulphate was not weighed.

	La_2O_3.	$La_2(SO_4)_3$.	$3SO_3 = 240.18$.	At. wt. La.
I.	1.0122	1.7592	0.7470	138.72
II.	1.1268	1.9581	0.8313	138.78
III.	0.94585	1.6437	0.69785	138.77
IV.	1.0675	1.8553	0.7878	138.73
V.	0.9030	1.5692	0.6662	138.78
VI.	1.1273	1.9589	0.8316	138.79
VII.	0.9407	1.6347	0.6940	138.78
VIII.	1.0455	1.8168	0.7713	138.78
IX.	1.1271	1.9586	0.8315	138.78
X.	1.3074	2.2720	0.9646	138.77
XI.	1.3389	2.3267	0.9878	138.77
XII.	1.2012	2.0874	0.8862	138.78

Taking the mean of the twelve determinations, we have for the atomic weight of lanthanum the value 138.77.

Attempt to Use the Oxalate Method.

An attempt was made to determine the atomic weight of lanthanum by decomposing the oxalate of lanthanum to the oxide, or by determining the oxalic acid in the oxalate by titration with a standard solution of potassium permanganate. This method had to be abandoned on account of the nature of lanthanum oxalate. It was found to be practically impossible to obtain lanthanum oxalate under conditions where it would give constant weight. The oxalate continued to lose in weight when dried for several days at 110; it further lost in weight when dried at 150°, and still further loss in weight was sustained when it was heated to 190°. A specimen which had been dried for a week at 190° gave off a very considerable quantity of water when heated from 230° to 240°, showing that considerable water had been retained by the oxalate above 200°.

The decomposition temperature of lanthanum oxalate was then studied. The salt was placed in a glass tube closed at one end and connected at the other with a wash-bottle closed by means of a ground-glass stopper. A solution of barium hydroxide was introduced into the bottle and protected from the carbon dioxide in the air by connecting it with a second similar bottle containing a solution of sodium hydroxide. Any carbon dioxide escaping from the decomposing oxalate was thus conducted through the solution of barium hydroxide. The oxalate was found to show incipient decomposition at 250°, which became very marked at somewhat higher temperatures.

Since the oxalate continued to give off water so close to its decomposition temperature it was not safe to completely dehydrate the salt and weigh it for the purpose of an atomic weight determination. The oxalate method for determining the atomic weight of lanthanum was, therefore, abandoned.

The result of the above investigation is, then, to show that

the atomic weight of lanthanum is 138.77 on the basis of oxygen $= 16$.

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May, 1902.

I. ON *p*-AZOXYBENZALDEHYDE.

BY F. J. ALWAY.

Kirpal[1] has shown that when nitrobenzaldehyde, dissolved in boiling water, is treated with zinc dust a yellowish-green solution results. From this solution he was unable to isolate the *p*-hydroxylaminebenzaldehyde, whose formation was to be expected in this case. This solution soon became turbid from the separation of a reddish-yellow solid. He found the completion of the change to be accelerated by blowing air through the solution, which was at the same time kept warm. This substance, when purified by recrystallization, melted at 194° and contained two aldehyde groups. As the elementary analysis and the molecular weight determination agreed with the formula of *p*-azoxybenzaldehyde and as Bamberger had shown that in many analogous cases aromatic hydroxylamines pass readily into the corresponding azoxy compounds the proof of the correctness of the above formula was considered sufficient. Had not Lucius and Brüning[2] recently patented a process for the preparation of *p*-azoxybenzaldehyde by another method which gave a substance differing in properties from that described by Kirpal, it would not have been considered necessary to further investigate the constitution of the compounds obtained by Kirpal's method as well as by the other.

While Bamberger, with his students (including Kirpal), was studying the various classes of *p*-hydroxylamine derivatives, Gatterman was investigating the electrolytic reduction, in concentrated sulphuric acid, of the aromatic nitro compounds. He found that when the primary reduction-product of *p*-nitrobenzaldehyde, *viz.*, N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime[3] was oxidized by ferric chloride solution, there

[1] Ber. d. chem. Ges., **30**, 1597.
[2] Patentblatt, **21**, 894 ; D. R. P., 111,384.
[3] Ber. d. chem. Ges., **29**, 3037.

$$NO_2 - \langle \rangle - CH - N - \langle \rangle - CHO$$
$$O$$
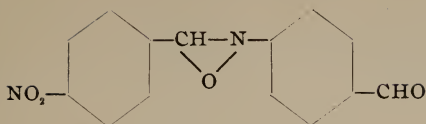
was formed *p*-nitrobenzaldehyde, together with a substance melting at 190° and not volatile with steam, and that the same non-volatile compound was produced when the above benzaldoxime was heated with dilute acids and the product distilled with steam. In both cases *p*-nitrobenzaldehyde was carried over by the steam.

Gattermann would have regarded this non-volatile substance as *p*-azoxybenzaldehyde had not Kirpal assigned to this latter compound a melting-point 4° higher (*viz.*, 194°). As the method of preparation used by Kirpal, viewed in the light of Bamberger's research on the oxidation of hydroxylamines to azoxy compounds when exposed to the air, seemed to fully identify the compound melting at 194° as *p*-azoxybenzaldehyde, Gattermann suggested that the compound melting at 190° might be the anhydride of *p*-hydroxylaminebenzaldehyde, *viz.*, $O(NH.C_6H_4.CHO)_2$.

Lucius and Brüning obtained the compound patented by them under the name of *p*-azoxybenzaldehyde (m. p. 180°) by the decomposition of its anilide (m. p. 167°), which, in turn, was produced by the treatment of *p*-nitrobenzylaniline with caustic alkalies.

If the compound obtained by the last method had the structure assigned to it, the compounds of Gattermann and Kirpal would probably be identical and both be a hydroxylamine anhydride, representing a new class of compounds. As will be seen from the calculated percentages and molecular weights given below, neither an elementary analysis nor a molecular weight determination would decide between the two formulæ, especially when the lowest percentage of hydrogen found in any analysis was 4.29 (Kirpal) and when the percentage of carbon was found, in all analyses, less than 66.00.

	Calculated for *p*-azoxybenzaldehyde, $C_{14}H_{10}O_3N_2$.	Calculated for the hydroxylamine anhydride, $C_{14}H_{12}O_3N_2$.
Molecular weight	254.0	256.0
C	66.1	65.6
H	3.9	4.7
N	11.0	10.9

In the hope of identifying *p*-azoxybenzaldehyde with one of the three above-mentioned compounds, a careful investigation of the subject has been undertaken in this laboratory. The results of my experimental work, up to the present, may be summarized as follows : The compound, described by Kirpal as *p*-azoxybenzaldehyde, melting at 194°, is identical with that mentioned by Gattermann, and when pure melts at 190° uncorr. Throughout the present article the name "*p*-azoxybenzaldehyde" is used to designate the compound melting at 190°, although the proof of its nature is not yet fully established. In addition to methods already published,[1] it may be obtained without difficulty by treating the secondary reduction-product of *p*-nitrobenzaldehyde with dilute acids or with ferric chloride solution, the yield being much greater than when the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is similarly treated. The last-mentioned compound, when treated with phenylhydrazine, yields the corresponding hydrazone, which readily reacts with more phenylhydrazine to form the hydrazones of *p*-nitrobenzaldehyde and *p*-azoxybenzaldehyde. The latter hydrazone is also formed by the action of phenylhydrazine upon *p*-nitrosobenzaldehyde. The formation of *p*-azoxybenzaldehyde by Kirpal's method depends upon the presence of oxygen and is favored by the presence of alkalies. It forms with aniline an anilide, with fuming nitric acid a mononitroazoxybenzaldehyde, and with phosphorus pentachloride an azoxybenzalchloride. When warmed with concentrated sulphuric acid to 100° it undergoes no change. Ordinary concentrated nitric acid, benzoyl chloride, acetyl chloride, acetic anhydride, and nitrous acid are without action upon it. The secondary reduction-product of *p*-nitrobenzaldehyde[2] is formed also by the electrolytic reduc-

[1] Ber. d. chem. Ges., **29**, 3037; **30**, 1597.
[2] *Ibid.*, **29**, 3037.

tion of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime. In this case a nitro compound is evidently reduced, in acid solution, to an azoxy compound. The action of aniline upon the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime and upon *p*-nitrosobenzaldehyde gives hydrazo and azo derivatives respectively, and not azoxy compounds. *p*-Nitrosobenzaldehyde, unlike the *p*-nitroso compounds investigated by Bamberger,[1] is changed by concentrated sulphuric acid into a polymeric compound.

EXPERIMENTAL.

Electrolytic Reduction of p-Nitrobenzaldehyde.

The exact conditions of reduction given by Gattermann[2] were followed. The *p*-nitrobenzaldehyde was dissolved in concentrated sulphuric acid and subjected to the action of a current of 6 volts and 2 to 3 amperes. The progress of the reaction was determined at frequent intervals by pouring a small quantity of the sulphuric acid solution into ice-water, filtering out the precipitate, which varied in color from yellow to red, thoroughly washing this on the filter with ice-water, in order to remove all adhering acid, and then, by the use of water and of pyridine, isolating the different compounds contained in the precipitate. Alcohol may not be used to extract the *p*-nitrobenzaldehyde as the primary reduction-product is soluble in the alcoholic solution of this aldehyde. Boiling water dissolves the unchanged aldehyde, while boiling pyridine dissolves the primary reduction-product. The red, secondary reduction-product remains after treatment with pyridine. At the end of about ten hours' further reduction, the primary product had entirely disappeared, and there remained only the red substance. When the pure primary product, recrystallized from pyridine, was subjected to further reduction under the conditions given above, it was likewise completely changed into the red substance in about ten hours.

[1] Ber. d. chem. Ges., **31**, 1513.
[2] *Ibid.*, **29**, 3037.

The Secondary Reduction-Product of p-Nitrobenzaldehyde.

The red substance does not melt below 330°, but seems to undergo decomposition at 220° to 230°. It is insoluble in the ordinary organic solvents and also in carbon disulphide, nitrobenzene, pyridine, phenol, and naphthalene. It dissolves in concentrated sulphuric acid, from which it may be recovered by pouring the solution into ice-water. When this solution is warmed to 100° the dissolved substance remains unchanged; but, when water is added to this warm solution, it is decomposed, yielding *p*-azoxybenzaldehyde. When boiled for half an hour with dilute sulphuric or hydrochloric acid, or for three hours with glacial acetic acid, the same compound is formed. By oxidation with ferric chloride solution, *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde are produced. No trace of *p*-nitrobenzaldehyde could be detected.

The oxidation of 1 gram of the primary reduction-product yielded 0.6 gram *p*-nitrosobenzaldehyde, 0.03 to 0.1 gram *p*-azoxybenzaldehyde, and 0.2 gram *p*-nitrobenzaldehyde. The small quantity of the last is probably due to the fact that it is appreciably soluble in cold water. The oxidation was effected by adding ferric chloride solution to the primary reduction-product suspended in water, while a rapid current of steam was led into the mixture. The *p*-azoxybenzaldehyde remained in the flask, suspended in the water. The *p*-nitrobenzaldehyde and the *p*-nitrosobenzaldehyde were carried over by the steam and collected in the receiver. The contents of the receiver were cooled, the flocculent precipitate filtered out, dried, and recrystallized from glacial acetic acid. The *p*-nitrosobenzaldehyde separated out completely when the solution was cooled, while the *p*-nitrobenzaldehyde remained dissolved.

The nitrosobenzaldehyde was filtered out and to the filtrate cold water was added in excess. Pure *p*-nitrobenzaldehyde separated out rapidly. Oxidation of 1 gram red reduction-product yielded 0.5 to 0.6 gram azoxybenzaldehyde and 0.25 to 0.35 gram *p*-nitrosobenzaldehyde. The distillate in this case, after the nitrosobenzaldehyde had been filtered out, was

extracted with ether. No trace of *p*-nitrobenzaldehyde was isolated from either the precipitate or the filtrate.

As no solvent was found from which it could be recrystallized, no analysis of the substance was made.

p-Azoxybenzaldehyde, $ON_2(C_6H_4.CHO)_2$.—This aldehyde has been obtained from three different compounds, the primary reduction-product, the secondary reduction-product, and *p*-nitrosobenzaldehyde, as well as by Kirpal's method described above.

p-Nitrosobenzaldehyde and the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime, when treated with phenylhydrazine, yield the hydrazone (see below) of the above aldehyde.

The solid remaining suspended in the water when the reduction-product of *p*-nitrobenzaldehyde was digested with dilute acid, or oxidized by ferric chloride solution, was filtered out and dried. In this condition it had a slight tinge of red. It was recrystallized from acetic acid after boiling several times with animal charcoal. It melted at 190°. It was then recrystallized from benzene four times. The melting-point remained constant. It crystallized in long, yellow needles from benzene or from dilute acetic acid. It is slightly soluble in hot water, cold alcohol, and ligroin, more soluble in boiling ligroin; it is readily soluble in benzene and glacial acetic acid, from which it crystallizes on cooling.

	Calculated for $C_{14}H_{10}N_2O_3$.	Found.
N	11.02	11.11

The molecular weight was determined by the freezing-point method, using naphthalene as the solvent.

	Calculated.	Found.	
Molecular weight	254	256	258

When boiled with dilute sulphuric or hydrochloric acid for three hours, it remained unchanged. It underwent no change when the solution in concentrated sulphuric acid was warmed to 100°, when boiled with ordinary concentrated nitric acid, with acetyl chloride or with benzoyl chloride, or when heated in a sealed glass tube with acetic anhydride to 100° for one hour. By oxidation with chromic acid in glacial acetic acid

solution, a gray substance, insoluble in ordinary solvents, was formed. This was not further investigated. It is doubtless *p*-azoxybenzoic acid, described by Kirpal.[1] When treated with zinc dust and acetic acid the *p*-azoxybenzaldehyde yields red crystals. Similar red crystals were observed at times among the yellow crystals obtained by recrystallizing the crude *p*-azoxybenzaldehyde, prepared as above described, from 90 per cent acetic acid. These have not yet been further investigated.

Preparation of p-Azoxybenzaldehyde by Kirpal's Method.[2]

As the melting-point of the aldehyde described by Gattermann remained constant at 190°, I prepared it by Kirpal's method, applying the results of Bamberger's investigation of the action of alkalies upon arylhydroxylamines in the presence of oxygen.[3]

Two grams of *p*-nitrobenzaldehyde were added to 150 cc. boiling water, and after one minute 12 grams zinc dust were added. The mixture was kept gently boiling for five minutes and then filtered under suction, using a Büchner funnel. The filtrate was placed in a stoppered flask and quickly cooled. A copious yellow precipitate separated out. This was found to be *p*-nitrobenzaldehyde, together with a little *p*-azoxybenzaldehyde. The greenish-yellow filtrate rapidly became turbid, and when air was passed through it a reddish-yellow precipitate formed. The reaction was complete at the end of twenty to twenty-four hours at 20°, and at the end of two to four hours when the temperature was kept between 90° and 100°. When the air was freed from acids (hydrochloric acid being present in greater or less degree in the air of a chemical laboratory), by first passing through wash-bottles containing potash solution and then through two containing distilled water to prevent any alkali solution being mechanically carried over, the precipitate was light-yellow in color with no trace of red. When the air was first passed through concentrated sulphuric acid, but not through alkaline solution, the precipi-

[1] Ber. d. chem. Ges., **30**, 1598.
[2] *Loc. cit.*
[3] *Ibid.*, **33**, 118, 271.

tate was reddish-yellow. The addition of acids to the filtrate caused a similar precipitate to form. When sodium hydroxide solution was added to the filtrate a deep-red coloration was produced, while a yellow flocculent precipitate rapidly separated out. When this mixture was kept agitated the reaction was complete at the end of half an hour. The filtered and dried precipitate obtained in the last operation was bright-yellow in color.

In order to determine the influence of the oxygen of the air upon the course of the reaction, the above experiments were repeated in an atmosphere of hydrogen which was purified by passing through a series of six wash-bottles, containing, respectively, potassium permanganate solution, concentrated sulphuric acid, pyrogallic acid in sodium hydroxide, and lastly, boiled distilled water. The liquid containing *p*-nitrobenzaldehyde in suspension was filtered directly into the digestion-flask, and the air in the latter was immediately replaced by hydrogen. The solution showed only traces of turbidity before the air had been expelled from the flask. The hydrogen was kept rapidly bubbling through the yellowish-green solution. After half an hour, at 20°, no appreciable change was noticed. Then the current of hydrogen was replaced by one of air, purified by passing through another set of wash-bottles (potassium permanganate solution, concentrated sulphuric acid, caustic soda solution). A yellow, flocculent precipitate soon began to form. The experiment was repeated (again in an atmosphere of hydrogen), keeping the contents of the digestion-flask boiling. At the end of thirty minutes very little solid had separated out. When sodium hydroxide solution was introduced into the yellowish-green filtrate, it at once became deep-red in color and a small quantity of a light-colored solid separated out in the course of half an hour. Then air was passed through the mixture another half hour. The filtered and dried solid in this case was reddish-yellow in color. The precipitate seems, from the above, to be red only when acids are present or when oxygen is absent.

All the precipitates thus obtained consisted essentially of

p-azoxybenzaldehyde. Those that were light-yellow in color dissolved in ligroin without residue. The others, when heated with this solvent, left a small quantity of red substance. Even after repeated recrystallization from acetic acid, and lastly from benzene, the yellow needles so obtained melted at 190°. The melting-point given by Kirpal (194°) is accordingly 4° too high. As the melting-point of the corresponding hydrazone was given by him as 230°, while I find it to be 228°, the error seems to have been in the thermometer used by him.

The residue of zinc dust remaining in the Büchner funnel, referred to above, was in one case dried and extracted with hot benzene. This filtrate, when treated with ligroin, yielded *p*-azoxybenzaldehyde. In a second case the residue was extracted several times with boiling water. On cooling, the yellow aqueous solution so obtained precipitated a reddish-yellow substance from which *p*-azoxybenzaldehyde and a smaller quantity of another compound, which crystallized from acetic acid in red needles, and melted at 222°, were obtained. The latter compound has not yet been further investigated.

p-Azoxybenzaldehydehydrazone,
$ON_2(C_6H_4.CH : N.NHC_6H_5)_2$.—This compound was obtained by the action of phenylhydrazine upon three different aldehydes, *viz.*, *p*-azoxybenzaldehyde, the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime and *p*-nitrosobenzaldehyde. The preparation from the second compound is described below. The preparation, when *p*-azoxybenzaldehyde is used, has already been described by Kirpal.[1] It was obtained from *p*-nitrosobenzaldehyde in the following manner: A mixture of phenylhydrazine and acetic acid was slowly added to a hot solution of the aldehyde in acetic acid. A rapid evolution of nitrogen at once took place, and a red solid separated out. As soon as the evolution of gas had ceased the reaction-mixture was cooled, the precipitate filtered out and washed on the filter with alcohol to remove the excess of phenylhydrazine. Then it was dried on the water-bath and recrystallized from pyridine. When recrystallized from benzene or from pyridine it forms orange-colored leaflets, which melt at 228° when

[1] Ber. d. chem. Ges., **30**, 1597.

heated rapidly. When heated slowly the compound undergoes decomposition at about 218° to 225°. While but slightly soluble in boiling pure alcohol, it dissolves to a considerable extent if the hydrazone of *p*-nitrobenzaldehyde is present.

An analysis was made of a portion of that obtained from the *p*-azoxybenzaldehyde.

	Calculated for $C_{26}H_{22}ON_6$.	Found.
N	19.3	19.2

A complete analysis was made of that obtained from *p*-nitrosobenzaldehyde.

	Calculated for $C_{26}H_{22}ON_6$.	Found.
C	71.9	71.6
H	5.1	5.5
N	19.3	19.0

p-Azoxybenzylideneaniline, $ON_2(C_6H_4.CH : N.C_6H_5)_2$. — *p*-Azoxybenzaldehyde was boiled for five minutes with an excess of aniline, the whole forming a clear solution. On cooling, a yellow crystalline substance separated out. This was well washed with ether to remove the unchanged aniline and then recrystallized from benzene. It forms large, yellow leaflets, melting at 185° to 192°. The melting-point, after repeated recrystallization, was no more definite. It dissolves with difficulty in ether, alcohol, ligroin, and cold benzene, but readily in the last solvent when hot.

	Calculated for $C_{26}H_{20}N_4O$.	Found.
N	13.8	13.8
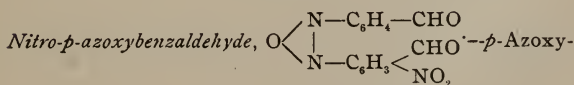
Nitro-p-azoxybenzaldehyde, $O{<}_{N-C_6H_3<\;}^{N-C_6H_4-CHO}{}^{CHO}_{NO_2}$ ·--*p*-Azoxy-

benzaldehyde was heated with fuming nitric acid until the evolution of brown vapors began. The solution was cooled and precipitated by water. The yellow precipitate was filtered out and recrystallized from glacial acetic acid. It forms yellow needles, melting at 171° to 172°. It is insoluble in water, but slightly soluble in ether and cold alcohol, and

readily soluble in hot acetic acid, from which it crystallizes on cooling.

	Calculated for $C_{14}H_9O_5N_3$.		Found.
N	14.0		13.9

p-Azoxybenzal Chloride, $ON_2(C_6H_4.CHCl_2)_2$.—The finely divided *p*-azoxybenzaldehyde (1 mol.) was mixed in a test-tube with an excess of phosphorus pentachloride (4 mols.). A lively reaction took place, hydrochloric acid escaping and the mass becoming partly liquid. As soon as the violent re-action had subsided the mixture was heated until it formed a clear red solution. This was poured into ice-water, yielding a red precipitate, which was filtered out, washed with water, dried on a porous plate, and recrystallized from ligroin. This compound forms orange-colored leaflets, melting at 115° to 116°.

	Calculated for $C_{14}H_{10}ON_2Cl_4$.	Found.	
		I.	II.
N	7.7	7.8	7.8
C	38.9	38.3	38.3

Action of Phenylhydrazine upon the N-p-Formylphenyl Ether of p-Nitrobenzaldoxime.

One gram of the recrystallized reduction-product was mixed with 12 grams absolute alcohol and an excess of phenylhydra-zine. This mixture was boiled for one minute. The liquid became red, the yellow reduction-product disappeared, and a red solid took its place. This was filtered out, thoroughly washed on the filter with ether in order to remove the excess of phenylhydrazine, dried, and recrystallized from pyridine. This compound forms dark-red leaflets, melting at 222°. It is insoluble in ether, benzene, acetone, carbon disulphide, and cold alcohol, and slightly more soluble in boiling alcohol and glacial acetic acid. It is readily soluble in boiling pyridine and nitrobenzene, from which it crystallizes on cooling.

	Calculated for $C_{20}H_{16}O_3N_4$.	Found.
N	15.6	15.5

This compound is, accordingly, the hydrazone of the above benzaldoxime derivative, and has the formula

$$O_2N.C_6H_4.CH\overset{O}{\overbrace{}}N.C_6H_4.CH:N.NH.C_6H_5.$$

The alcoholic filtrate from the above hydrazone was treated with water. A brown precipitate formed, which was filtered out, dried on the water-bath, and treated with cold benzene.

The greater part dissolved in the benzene. The orange-colored residue was filtered out and recrystallized from benzene. It proved to be the hydrazone of *p*-azoxybenzaldehyde. The benzene, with which the crude precipitate had been treated, was evaporated to dryness and the residue recrystallized from glacial acetic acid. The red needles thus obtained were identified as the hydrazone of *p*-nitrobenzaldehyde, melting at 155°.

When aqueous instead of absolute alcohol was used, none, or only traces of the hydrazone melting at 222° was obtained, while there was a good yield of the hydrazones of *p*-nitrobenzaldehyde and *p*-azoxybenzaldehyde.

Anilide of p-Aldehydohydrazobenzene, $C_6H_5.NH.NH.C_6H_4.$ $CH=N.C_6H_5.$—The primary reduction-product was heated with excess of aniline until the crackling, produced by the escaping steam, ceased (two to three minutes). On cooling, crystals separated out and the mixture with aniline became solid. This mixture was first washed several times with dilute hydrochloric acid in order to remove the unchanged aniline, then filtered, dried on a porous plate, and lastly boiled with ligroin twice, in order to remove the anilide of *p*-nitrobenzaldehyde. The greater part of the reaction-mixture remained undissolved. The residue was several times recrystallized from benzene.

This compound forms orange-colored leaflets melting at 183° to 186°. It dissolves but slightly in ligroin, alcohol, and acetone, but very readily in hot benzene, from which it separates on cooling.

|	Calculated for $C_{19}H_{17}N_3$.	Found.
C	79.4	79.3
H	5.9	5.5
N	14.6	14.3

Reaction of p-Nitrosobenzaldehyde with Concentrated Sulphuric Acid.

p-Nitrobenzaldehyde (1 gram) was gradually added to concentrated sulphuric acid (6 cc.), a deep violet-colored solution being formed. After standing ten minutes the solution was poured into ice-water. A red precipitate was at once formed. This was filtered off, thoroughly washed on the filter with water, and then twice recrystallized from glacial acetic acid.

This compound forms a dark-red powder melting at 204° to 206°. It is insoluble in water, ether and ligroin, only slightly soluble in hot benzene, hot alcohol, and cold glacial acetic acid, but readily soluble in the last when hot.

	Calculated for $(C_7H_5O_2N)x.$	Found.
C	62.2	61.8
H	3.7	3.8
N	10.4	10.3

Bamberger's investigation of the action of concentrated sulphuric acid upon nitrosobenzene and other nitroso compounds,[1] which yield hydroxylamine derivatives of the formula

$$C_6H_5-\underset{\underset{OH}{|}}{N}-C_6H_4.NO,$$
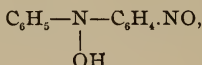
would have led me to assign the formula

$$C_6H_4\begin{cases} CHO \\ N.OH \end{cases}$$
$$C_6H_3-NO$$
$$\qquad\qquad CHO$$
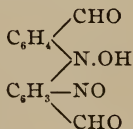
to this compound, had he not found that compounds in which the para-position was occupied by another group or by a halogen atom, were incapable of this aldol condensation.

This compound will be further investigated in this laboratory.

[1] Ber. d. chem. Ges., **31**, 1513.

Action of Aniline upon p-Nitrosobenzaldehyde.

Benzeneazobenzylideneaniline, $C_6H_5.N : N.C_6H_4.CH : N.C_6H_5.$
—A mixture of aniline (2 mols.), acetic acid (1 mol.), and
p-nitrosobenzaldehyde (1 mol.) was boiled for a few minutes.
The product of the reaction, which solidified on cooling, was
twice recrystallized from aqueous alcohol and then once from
ligroin. This anilide consists of very small orange-colored
needles, melting at 125° to 130°. It is but slightly soluble in
cold alcohol, ligroin, and benzene, more readily soluble in
boiling ligroin, and very soluble in hot alcohol and benzene.

	Calculated for $C_{19}H_{15}N_3$.	Found.
N	14.7	14.8

Benzeneazobenzaldehyde, $C_6H_5.N : N.C_6H_4.CHO.$—The last-
described compound was dissolved in boiling dilute acetic acid.
A small quantity of brown oil separated out. The solution
was poured off from the oil. On cooling, crystals separated
out, which were filtered off and recrystallized from alcohol.

This aldehyde crystallizes from alcohol and from dilute
acetic acid in brownish-red, glistening leaflets, melting at 116°.
It is but slightly soluble in cold alcohol and ligroin, more
soluble in benzene, glacial acetic acid, and hot alcohol.

	Calculated for $C_{13}H_{10}ON_2$.	Found.
C	74.3	74.6
H	4.8	5.0
N	13.3	13.4

The hydrazone of the above aldehyde was prepared by
treating the hot solution of the aldehyde in acetic acid with
phenylhydrazine. A red precipitate at once appeared, which
was recrystallized from glacial acetic acid. It forms long, red
needles, melting at 154°.

	Calculated for $C_{19}H_{16}N_4$.	Found.
N	18.7	18.5

The aldehyde, obtained from m-nitrobenzaldehyde by
methods analogous to those used in the conversion of p-nitro-

benzaldehyde into the compound melting at 190°, melts at 129° and yields a hydrazone, melting at 198°. Both this compound and that obtained by the action of caustic alkalies upon p-nitrobenzylaniline are still under investigation in this laboratory.

UNIVERSITY PLACE, April 16, 1902.

Contributions from the Chemical Laboratory of the University of Nebraska.

III. A CONTRIBUTION TO THE CHEMISTRY OF THE AROMATIC GLUTARIC ACIDS.

BY S. AVERY.

Vol. XX., p. 509, of this JOURNAL contains an article by Rosa Bouton and the writer '' On Phenylglutaric Acid and Its Derivatives.'' Up to this time only two aromatic glutaric compounds were given in chemical literature, *i. e.*, β-phenylglutaric acid[1] and its silver salt. The opening paragraph of this article closes with the words: '' We have accordingly entered the study of these acids, hoping to widen our knowledge of the subject in general, and especially to determine the influence of the phenyl groups on melting-points and the formation of anhydrides.'' The article closes with an account of an unsuccessful attempt to prepare the then unknown α-phenylglutaric acid. The closing sentence reads: '' We hope to prepare α-phenylglutaric acid by another method.''

Vol. XX., p. 516, of this JOURNAL contains an article by Mary L. Fossler and the writer, describing a successful attempt to prepare α-methyl-β-phenylglutaric acid. The closing sentence reads: '' We shall investigate this subject further as well as the homologues and isomers of the compounds described.''

During the four years that have elapsed since the above was written, the writer and his students have investigated the subjects above outlined. As, however, other investigators have had occasion to enter this field, it seems desirable to publish, without longer delay, the results already obtained. These results are here given in the form of a communication from the writer and his students.

[1] J. prakt. Chem., [2], **35**, 352.

The following table gives the melting-points of the acids, anhydrides, and anilic acids to be found in the literature of the subject:

	Acid.	Anhydride.	Anilic acid.
β-Phenylglutaric	137°.5–138°.5[1]	105°[3]	139°[3]
	138°[2]	105°[4]	139°[4]
	140°[4]		
α-Phenylglutaric	82°–83°[5]	95°[5]	
α-Methyl-β-phenylglutaric	122°[6]	74°[7]	
	125°[7]		
p-Tolylglutaric	165°–167°[8]	153°[8]	194°–196°[8]
β-m-Nitrophenylglutaric	205°–206°[9]	170°.5[10]	160°[10]
	206°[10]		
β-p-Nitrophenylglutaric	236°[11]		120°–121°[12]
	237°[12]	122°.5[12]	
β-o-Nitrophenylglutaric (?)	175°[12]		

EXPERIMENTAL PART.

β-p-TOLYLGLUTARIC ACID.

BY S. AVERY AND H. C. PARMELEE.

The method used in preparing this acid may be outlined as follows :

I. Preparation of p-tolylacrylic ester.

II. Condensation of p-tolylacrylic ester with sodium malonic ester.

III. Saponification in acid solution of the resulting tricarboxylic ester.

p-Methylbenzaldehyde was condensed with acetic ester according to the method of Claisen.[13] The amount of crude ester distilling between 260° and 280° represented 1.175 times the

[1] Michael : J. prakt Chem., [2], **35**, 352.
[2] Vorländer und Kohlmann : Ber. d. chem. Ges., **32**, 1879.
[3] Hermann und Vorländer : Centrbl., 1899, 730.
[4] Avery and Bouton : This JOURNAL, **20**, 509.
[5] Fichter and Merckens : Ber. d. chem. Ges., **34**, 4175.
[6] Avery and Fossler : This JOURNAL, **20**, 516.
[7] Carter and Lawrence : Chem. News, 1900, p. 253.
[8] Avery and Parmelee : This JOURNAL, **28**, 49.
[9] Knoevenagel : Ann. Chem. (Liebig), **303**, 235.
[10] Avery and Gere : This JOURNAL, **28**, 51.
[11] Knoevenagel : Ann. Chem. (Liebig), **303**, 239.
[12] Avery and Beans : This JOURNAL, **28**, 55.
[13] Ber. d chem. Ges., **23**, 976.

weight of the aldehyde employed. A small sample, on saponification, yielded nearly pure *p*-tolylacrylic acid, identical in all respects with the acid described by Kröber.[1] The *p*-tolylacrylic ester was condensed with sodium malonic ester and the resulting carboxylic ester saponified with hydrobromic acid. The product of the reaction was extracted with boiling water. On cooling, crystals of β-tolylglutaric acid separated out. These were recrystallized first out of a mixture of acetic and petroleum ethers and then out of water. The pure compound forms transparent, oblique prisms, melting at 165° to 167°, soluble in acetic ester, hot water, and chloroform, less soluble in ether, practically insoluble in benzene, petroleum ether, and in water at 0°.

Analysis :

0.2004 gram substance gave 0.4776 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_{12}H_{14}O_4$.	Found.
C	64.86	65.01
H	6.35	6.65

Salts of p-Tolylglutaric Acid.

Nearly all the salts described in this paper were formed by precipitation from the ammonium salt.

Silver Salt.—White amorphous powder.

Analysis :

0.2413 gram salt gave 0.1191 gram Ag.

	Calculated for $C_{12}H_{12}O_4Ag_2$.	Found.
Ag	49.46	49.35

Copper Salt.—Green crystalline powder.

Analysis :

0.1627 gram salt gave 0.04279 gram CuO.

	Calculated for $C_{12}H_{12}O_4Cu.H_2O$.	Found.
Cu	21.04	21.08

Calcium Salt.—White crystalline powder.

Analysis :

0.0515 gram salt gave 0.0109 gram CaO.

[1] Ber. d. chem. Ges., **23**, 1033.

	Calculated for $C_{12}H_{12}O_4Ca$.	Found.
Ca	15.384	15.118

β-p-Tolylglutaric Anhydride.—This compound may be prepared by heating the acid above its melting-point or by treating the acid with hot acetyl chloride. The latter method is the more convenient. The acetyl chloride is evaporated off on the water-bath and the residue extracted with dry benzene. On the addition of dry petroleum ether to the benzene solution, the anhydride separates out in feathery crystals which melt at 153°.

β-p-Tolylglutaranilic Acid.—The anhydride just described reacts with aniline in benzene solution to form the anilic acid. The acid may be obtained in pure condition by recrystallizing from alcohol. Glistening white needles melted at 194° to 196°. A silver salt of the anilic acid was analyzed.

0.1972 gram salt gave 0.0523 gram Ag.

	Calculated for $C_{18}H_{18}O_3NAg$.	Found.
Ag	26.69	26.52

β-p-Tolylglutaranil.—When the acid just described is heated above its melting-point, water is given off and a slight decomposition takes place. On cooling, the liquid solidifies to a crystalline mass. By recrystallizing from alcohol long, sharp needles are obtained, which melt at 174°.5.

Analysis :

0.2188 gram substance gave 10.7 cc. N at 27°.5 and 730 mm.

	Calculated for $C_{18}H_{17}O_2N$.	Found.
N	5.109	5.164

β-m-NITROPHENYLGLUTARIC ACID.

By S. Avery and M. C. Gere.

While the investigation of the nitrophenylglutaric acids was in progress, Knoevenagel[1] published his synthesis of the meta and para acids. He did not, however, prepare derivatives. Hence our work was continued. We prepared the acid by saponifying in acid solution the tricarboxylic ester formed

[1] Ann. Chem. (Liebig), **303**, 235.

by the action of sodium malonic ester on *m*-nitrocinnamic ester.

The tricarboxylic ester was placed in an Erlenmeyer flask and dilute hydrobromic acid added. A quantity of broken glass and scrap platinum was then dropped in to prevent bumping, and the flask placed on a thin piece of asbestos over a wire gauze. It was then connected with the inner tube of a Liebig condenser instead of the ordinary return flow, and heated gently with the flame. After some time a brown, tarry-looking oil settled to the bottom of the flask, but was gradually dissolved. After heating about eight hours the saponification was completed. At the end of the operation most of the acid was in the form of a gray precipitate in the bottom of the flask. As the liquid cooled, more of the acid separated out. The precipitate was filtered off on a Witt plate as a yellowish-gray, amorphous mass. It was then washed with water, and the washings, together with the mother-liquor, evaporated down, and the acid which crystallized out was filtered off. The entire yield was then washed and crystallized from weak alcohol, washed with cold water, and dried in a vacuum.

Part of the acid was purified by converting into the anhydride by means of acetic anhydride, and recrystallizing the resulting anhydride several times, then converting it back into the acid by dissolving in dilute alcohol. The acid thus obtained was distinctly crystalline and almost white. Its melting-point was 205° to 206°. It was found to be easily soluble in alcohol and ether, less soluble in water, very little, if at all, soluble in benzene, chloroform, and petroleum ether.

Analysis :

0.23777 gram acid gave 0.09494 gram H_2O and 0.45628 gram CO_2.

	Calculated for $C_{11}H_{11}O_6N$.	Found.
C	52.17	52.33
H	4.35	4.43

Salts of β-*m*-Nitrophenylglutaric Acid.

Silver Salt.—White amorphous powder.

Analysis :

0.3329 gram silver salt gave 0.1533 gram Ag.

	Calculated for $C_{11}H_9O_6NAg_2$.	Found.
Ag	46.22	46.05

Calcium Salt.—Calcium chloride produces no precipitate with the ammonium salt of β-*m*-nitrophenylglutaric acid, but on adding alcohol the calcium salt is readily thrown down as a white, flaky precipitate, which is very distinctly crystalline.

Analysis :

0.2005 gram calcium salt gave 0.03615 gram CaO.

	Calculated for $C_{11}H_9O_6NCa.H_2O$.	Found.
Ca	12.916	12.869

Barium Salt.—To a partial solution of the acid in water a solution of barium hydroxide was added from a burette until a faint reaction was given with phenolphthalein. The acid went into solution, but seemed to crystallize out again, so an excess of barium hydroxide was added, and carbon dioxide passed in to precipitate the excess. The solution was then filtered and evaporated on a water-bath. By cooling in a freezing-mixture and constantly stirring, a very finely crystalline, white precipitate separated out. It was filtered, washed, and analyzed.

Analysis :

0.20055 gram barium salt gave 0.1033 gram $BaCO_3$.

	Calculated for $C_{11}H_8O_6NBa$.	Found.
Ba	35.36	35.7

Copper Salt.—Green amorphous powder.

Analysis :

0.20035 gram copper salt gave 0.0402 gram Cu.

	Calculated for $C_{11}H_9O_6NCu$.	Found.
Cu	20.114	20.06

β-m-Nitroglutaric Anhydride.—The anhydride was made by the action of boiling acetic anhydride on the acid. While still hot, a small amount of benzene was added, though not

enough to make two layers. The solution was then filtered
and cooled in a freezing-mixture. White, glistening crystals
separated out. Upon filtering off and drying, they were found
to be very light and silky and, apparently, quite pure, melt-
ing sharply at 170°.5. They are insoluble in benzene and
petroleum ether, but soluble in alcohol, being changed by it to
the acid. They were insoluble in water, which acts on them
not at all, or with great difficulty.

Several nitrogen determinations of the anhydride were
made, but in each case the amount found was from 0.3 to 0.4
per cent too high. This may be due to the fact that the an-
hydride contained some impurity which eluded detection, but
which evidently did not affect the melting-point, which was
quite sharp. However, there is no doubt that the anhydride
was obtained, since it yielded β-*m*-nitrophenylglutaranilic
acid.

β-m-Nitrophenylglutaranilic Acid.—This acid was made by
the action of the anhydride on aniline in benzene solution. It
was found that a very pure, white, flaky, crystalline precipi-
tate could be obtained by dissolving the anilic acid in 50 per
cent alcohol and then adding petroleum ether until a few
white specks appeared in the liquid or until there was a very
slight milkiness. Upon standing a short time the precipitate
gradually separates out in a very pure condition. The anilic
acid melts at 160° C. It is soluble in alcohol, insoluble in
petroleum ether and benzene.

	Calculated for $C_{17}H_{16}O_5N_2$.	Found.
N	8.59	8.402

Silver Salt of Anilic Acid.—When made in the usual way
by neutralizing with ammonia and precipitating with an ex-
cess of silver nitrate, the amount of silver proved to be too
large, upon analysis. This was due to the difficulty in wash-
ing out the excess of silver nitrate, on account of the ex-
tremely gelatinous character of the precipitate formed by
the anilic acid; the precipitate closely resembles alumina. It
was therefore prepared as follows: Equivalent amounts
of silver foil and anilic acid were weighed out. The silver

was converted into silver nitrate and the anilic acid into the ammonium salt by the usual methods. The two solutions, now rather dilute, were mixed together and then heated to boiling. It was then cooled in a freezing-mixture and the gelatinous precipitate formed at once. This was then filtered and washed in the usual way. The salt thus formed was chemically pure, as shown by the analysis.

It is fairly stable when dried below 100°, but when heated to 120° it rapidly becomes black. It is not very readily affected by light.

Analysis :

0.1021 gram silver salt gave 0.0253 gram Ag.

	Calculated for $C_{17}H_{15}O_5N_2Ag$.	Found.
Ag	24.79	24.78

β-p-NITROPHENYLGLUTARIC ACID.

BY S. AVERY AND HAL. T. BEANS.

Nitration of β-Phenylglutaric Acid.

Twenty-two grams β-phenylglutaric acid, dry and finely pulverized, were gradually added in small portions, to 200 cc. fuming nitric acid, cooled to zero, in a freezing-mixture. The temperature was kept below 10°, remaining between 8° and 10° during the greater portion of the experiment. When all had been added, the reaction-mixture was poured into ice-water, causing a finely-divided, light-yellow precipitate to separate. This was filtered off and washed free from nitric acid with cold water. It was then digested with hot water, filtered, and again digested.

By this treatment two products are obtained. One is practically insoluble in hot water and melts sharply at 237° after recrystallization from dilute alcohol. It was identified as β-paranitrophenylglutaric acid. From 22 grams β-phenyl-glutaric acid, 18 grams of the pure paranitro acid were obtained, and some later experiments gave even higher yields. The other compound is soluble in hot water and crystallizes out, on standing, in fine, light-yellow crystals, which, after recrystallization from hot water, melt at 175°. This product

has not, as yet, been investigated, but is probably β-orthonitrophenylglutaric acid. Under the conditions of nitration given, the amount of this compound formed does not exceed 10 per cent of the phenylglutaric acid used.

In working with nitric acid of different concentrations it was observed that, as the strength of acid increased and the temperature rose, the amount of water-soluble compound increased. This suggests the similar result obtained in nitrating cinnamic acid, when, with increasing concentration of the nitric acid, the proportion of orthonitrocinnamic acid increases.

To prove that the nitro group occupies the para position, some of the acid was oxidized to the corresponding nitrobenzoic acid by heating with chromic acid in sulphuric acid solution. The resulting product was extracted with ether, in which the nitroglutaric acid is insoluble, while nitrobenzoic acid dissolves. On evaporating the ether a solid was obtained which, after crystallizing from alcohol, melted sharply at 238°. Paranitrobenzoic acid melts at 238°, thus proving the nitroglutaric acid to be a para compound.

β-p-Nitrophenylglutaric acid forms almost colorless, hard, short prisms, melting sharply at 237°. It is soluble in alcohol, ethyl acetate, and glacial acetic acid, very difficultly soluble in hot water and benzene, and insoluble in chloroform, ether, and ligroin.

Salts of β-p-Nitrophenylglutaric Acid.

The *silver salt* was made in the usual way. It forms a nearly white, curdy precipitate which, when dry, is very stable in the light.

Analysis:

0.6190 gram salt gave 0.2853 gram Ag.

	Calculated for $C_{11}H_9NO_6Ag_2$.	Found.
Ag	46.22	46.09

The *calcium salt* was made by neutralizing the acid with calcium hydroxide at boiling temperature. The solution was concentrated and alcohol added, when the salt precipitated

out in white, glistening flakes. The salt is soluble in water but insoluble in alcohol.

Analysis:

After drying the salt at 100°, the calcium was determined by igniting and weighing as the oxide.

0.2061 gram salt gave 0.0387 gram CaO.

	Calculated for $C_{11}H_9NO_6Ca$.	Found.
Ca	13.74	13.41

The salt may have retained some water.

The *barium salt* was prepared in a similar way. It separates as a white, silky, crystalline precipitate and is somewhat less soluble than the calcium salt.

Analysis:

The barium was determined by igniting and weighing as the carbonate.

0.1530 gram salt gave 0.0780 gram barium carbonate.

	Calculated for $C_{11}H_9NO_6Ba$.	Found.
Ba	35.36	35.46

β-p-Nitrophenylglutaric anhydride is formed by dissolving the acid in boiling acetic anhydride and then adding dry benzene. On cooling, it separates in fine, light-yellow crystals. After recrystallization from acetic ether it forms clear crystals of slightly yellowish color, melting at 122°.5. It is comparatively stable, water acting on it with difficulty. It is soluble in acetic ether, difficultly soluble in hot benzene, and insoluble in cold benzene. It dissolves in hot, dilute alcohol, being converted back into the acid which separates, on cooling, in almost colorless, glistening crystals, melting at 237°.

Analysis:

0.1093 gram anhydride gave 0.2265 gram CO_2 and 0.0390 gram H_2O.

0.2447 gram anhydride gave 13.9 cc. N at 26° and 728 mm.

	Calculated for $C_{11}H_9NO_5$.	Found.
C	56.14	56.51
H	3.87	3.98
N	5.95	6.02

β-p-Nitrophenylglutaric Dimethyl Ester.—The dimethyl ester was prepared by treating the anhydride in absolute methyl alcohol, with dry gaseous hydrochloric acid. After saturation with hydrochloric acid, the excess of alcohol was evaporated off on the water-bath and the residue cooled and stirred, when it solidified into a crystal mass. This was washed with water, dried, and recrystallized from ethyl alcohol. The ester forms large, almost colorless, plates, which melt very sharply at 62°. It is insoluble in water but very soluble in alcohol.

Analysis:

I. 0.2033 gram ester gave 9.6 cc. N at 21° and 729.8 mm.

II. 0.2664 gram ester gave 12.7 cc. N at 24° and 734.7 mm.

	Calculated for $C_{13}H_{15}NO_6$.	Found. I.	II.
N	4.98	5.18	5.14

β-p-Nitrophenylglutaranilic Acid.—One gram β-p-nitrophenylglutaric anhydride was dissolved in about 15 cc. of hot, dry benzene with the addition of a little alcohol-free acetic ether. To the hot solution was added 0.416 gram freshly distilled aniline dissolved in a little benzene, and the mixture brought to boiling. On cooling, needle crystals of slightly yellow color separated out. These melt at 105° with the liberation of the vapor of benzene. After crystallizing from dilute alcohol, the crystals are light, glistening flakes, melting at 120° to 121°. The melting-point is not further changed by crystallizing from ethyl acetate. It must be noted here that the melting-point is not constant unless the heat is very carefully applied, since the substance very readily loses water to form the anil.

Silver Salt of the Anilic Acid.—The silver salt is a white, gelatinous precipitate. It is stable when heated to 120° and does not readily blacken in the light.

Analysis:

0.1336 gram salt gave 0.0332 gram Ag.

	Calculated for $C_{17}H_{15}N_2O_5Ag$.	Found.
Ag	24.79	24.85

β-p-Nitrophenylglutaranil.—On heating the anilic acid in a crucible supported inside a larger crucible, it first melts and then gives off water vapor, forming a clear, brownish liquid. Toward the end of the reaction there is a slight further decomposition, as shown by the liberation of a heavy vapor having the odor of burning nitrogenous matter. At this point the heating is stopped and the contents of the crucible allowed to cool. There is obtained a clear, brittle glass, soluble in acetone and glacial acetic acid. From either of these solvents the anil crystallizes in fine, white needles, which melt at 203°.

THE ACTION OF FUSED SODIUM DIOXIDE ON METALS.

[SECOND PAPER.[1]]

BY WM. L. DUDLEY.

1. Nickelo-Nickelic Oxide, Ni_3O_4. — On heating nickelo-nickelic hydrate (prepared by fusing sodium dioxide in a nickel crucible) to 240° C., a black, lusterless, amorphous powder remains, consisting of nickelo-nickelic oxide, Ni_3O_4. It is hygroscopic and absorbs 7.4 per cent of water from the air at 30° C., but it loses it completely at 110° C. It dissolves in hydrochloric acid with the evolution of chlorine, in sulphuric and nitric acids with the evolution of oxygen. It is non-magnetic.

Daubigny[2] describes a gray, non-magnetic solid, of metallic appearance, obtained by passing oxygen over $NiCl_2$ at 350° to 440° C., as Ni_3O_4, but he gives no results of analysis, and his description does not accord with that of Ni_3O_4, prepared by heating $Ni_3O_4,2H_2O$, as described above.

2. Magnetic Ferric Hydrate, Fe_2O_3,H_2O.[3]—Iron is very

[1] The publication which the author considers the "first paper" under the above title appeared in the *Journal of the American Chemical Society*, 18, 901, with the caption "Nickelo-Nickelic Hydrate, $Ni_3O_4,2H_2O$."

[2] Compt. rend., 87, 1082.

[3] A paper, describing the action of fused sodium dioxide on iron, was read by the author before the Chemical Section at the Boston meeting of the A. A. S., in 1898, but it was not then presented for publication, since the investigation was incomplete.

rapidly attacked by fused sodium dioxide, especially if it be heated to bright redness. An ordinary sheet-iron crucible will rarely withstand more than one or two fusions without perforation. Clippings of iron put into the crucible will protect it to some extent and at the same time hasten the action of the sodium dioxide.

If the fusion is kept at a bright-red heat for thirty minutes the action will usually be complete, but at dull redness some of the sodium dioxide will remain undecomposed for three and a half hours, or longer.

On treating the fused mass with water, a crystalline iron compound remains undissolved. If manganese be present in the iron the solution will have a purple color, due to the presence of sodium permanganate produced by the oxidizing action of the sodium dioxide, provided the temperature of bright redness has been employed in making the fusion ; but if it be made at a very high red heat the solution will be colorless, owing to the decomposition of the sodium permanganate, while at a dull red heat sodium manganate will be formed and the solution will consequently have a green color.

The iron compound consists of tabular, scale-like crystals, with outlines too indefinite for an accurate determination of their form. The color varies from reddish-brown to rich garnet. When the crystals are larger they are dark-red, frequently appearing to be black. The streak is brown. The specific gravity is 3.8 at 27° C.

The crystals are decidedly magnetic. When heated to redness they sinter together, but the residue is still magnetic.

The compound, prepared as described above, was freed from alkáli by washing first by decantation and then in a Soxhlet apparatus until no alkalinity could be detected by means of phenolphthalein in the washings. This result was usually attained in about fifty hours. The compound was then dried over calcium chloride, since there was found to be a slight loss of water at 100° C.

Analysis of the compound proved that the formula was Fe_2O_3,H_2O, as shown below :

|	Calculated for Fe_2O_3,H_2O.	Found. I.	II.
Fe	62.92	62.86	62.96
H_2O	10.11	9.94	10.09

The presence of ferrous oxide could not be detected.

After heating the crystals to low redness the residue, though magnetic, proved to consist of Fe_2O_3, as shown by the following analysis :

	Calculated for Fe_2O_3.	Found.
Fe	70.00	70.03

Several authors[1] have described the preparation of Fe_2O_3, H_2O by various methods, involving the use of the alkalies, fused or in solution, but its properties, as described by them, differ very materially from those of the compound made by fused sodium dioxide.

The crystalline hydroxide is formed during the fusion with the sodium dioxide and not by the decomposition of sodium ferrite (Fe_2O_3,Na_2O) when water is added. If sodium ferrite is formed during the fusion it is decomposed as the temperature rises and the crystals of Fe_2O_3,H_2O are formed in the crucible. On treating the fused mass with water the crystals remain intact. The formation of the hydroxide in the fusion is accounted for by the presence of sodium hydroxide, which usually varies from 8 to 25 per cent in all samples of sodium dioxide. The reaction may be represented as follows :

$$2Fe + 3Na_2O_2 + 2NaOH = Fe_2O_3,H_2O + 4Na_2O.$$
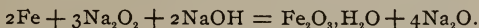
I am indebted to Mr. W. P. Connell for the analytical work done in the investigation of this compound.

3. Gold.—Fused sodium dioxide attacks gold very rapidly and leaves it in a spongy state. The gold seems to be oxidized, but the oxide formed decomposes at the temperature of fusion of the sodium dioxide and does not re-form on cooling, therefore the gold remains in the form of sponge.

Au_2O_3 gives off some oxygen at 110° C., and at 160° C. AuO

[1] Muck : Ztschr. Chem., [2], 4, 41 ; P. de Saint Gilles : Ann. chim. phys., [3], 46, 47 ; Brunck and Graebe : Ber. d. chem. Ges., 13, 725 ; Schiff : Centrbl., I., 1860, p. 1768 ; Rousseau and Bernheim : Compt. rend., 106, 1530 ; Rousseau : Compt. rend., 110, 1032 ; van Bemmelen and Klobbie : J. prakt. Chem., 46, 497–529.

remains, which, in turn, is decomposed at 250° C., leaving metallic gold.

4. Silver.—When sodium dioxide is fused in a silver crucible the metal is so rapidly attacked that a vessel of ordinary thickness will be perforated after three or four fusions, even if scraps of silver be added. When the fusion is conducted at full red heat, the action ceases in from twenty to thirty minutes, and the fused mass will be filled with needle-shaped crystals. On treatment with water the silver compound remains, for the most part, undissolved, although the alkaline solution will contain some silver.

An endeavor was made to wash the compound in a Soxhlet extractor, but it was found that the glass of the apparatus was slowly attacked and that the silver compound slowly dissolved. The washings gradually became wine-colored and dichroic, and finally a black precipitate separated. The washings maintained decided alkalinity. In order to determine the result of continued washing, this process was carried on daily for about three months, at the end of which time the washings were still alkaline and wine-colored, although the dichroic effect had gradually diminished. The residue in the thimble was comparatively small and quite black. The glass of the extractor was decidedly attacked and deeply stained.

The precipitate which separated from the washings was black and amorphous. It was readily attacked by nitric acid, which dissolved it, leaving a small quantity of white residue. Analysis gave it the following composition :[1]

Ag_2O	84.25
Na_2O	2.67
SiO_2	13.22

[1] It cannot be asserted that this is a definite silicate, since the existence of silver silicate is uncertain. The analysis, however, indicates that it may be a complex double silicate having the formula $17Ag_2O,2Na_2O,10SiO_2$ ($Ag_{34}Na_4Si_{10}O_{39}$), which would have the following percentage composition :

Ag_2O	84.44
Na_2O	2.67
SiO_2	12.89

The compound sustained the following losses on heating :

105° C.	1.00
250° C.	2.78
Redness	5.52

This loss was oxygen, doubtless from the Ag_2O in the compound, and should be 5.84 per cent, if all of the silver oxide it contained were thus reduced.

The wine-colored solution from the extractor was found to contain 1 part of solid matter in 2777 parts of water, at 20° C. On evaporating to dryness a black, scaly residue remained, 58.24 per cent of which could be redissolved in water. It was partly soluble in acids. The residue was found to contain :

Ag	20.66
SiO_2	29.07
Na_2O	21.93

together with various impurities from the eroded glass.

The plan of washing out the alkali from the silver compound had to be abandoned and the following method was adopted : After dissolving the fusion-product in water, the solution was decanted from the crystalline silver compound, more distilled water was poured over it, and a drop or two of phenolphthalein was added as an indicator. The excess of alkali was then carefully neutralized with acetic acid, the silver compound filtered out and washed with cold distilled water. It was found that filter-paper was attacked by the compound, and, therefore, a Gooch crucible of platinum, with platinum sponge as the filtering medium, was employed.

The crystals possess a gray and somewhat metallic luster. They are, apparently, flattened and elongated prisms, some of them showing oblique termination and suggesting monoclinic symmetry.

The compound was dried in a desiccator over calcium chloride, and on analysis was found to contain :

Ag	97.99
O	1.82

Assuming the crystals to be a mixture of silver oxide and metallic silver, the proportion would be :

$$Ag_2O \qquad\qquad 26.31$$
$$Ag \qquad\qquad 73.69$$

But 1.8245 per cent, which was the actual amount of oxygen found in the crystals, corresponds so closely to the theoretical proportion of oxygen which there would be in Ag_8O—*i. e.*, 1.825 per cent, that further investigation was made to determine this point. The crystals were digested with strong ammonium hydroxide (which readily dissolves Ag_2O) for twenty-four hours, filtered, washed, and dried over calcium chloride. On analysis the substance was then found to contain only 0.175 per cent of oxygen, showing that about nine-tenths of the silver oxide had been dissolved and that the crystals probably consist of a mixture of silver oxide (Ag_2O) and silver; or, that if the oxide Ag_8O (which has never been described) does exist, it is decomposed by ammonium hydroxide into silver oxide and silver, which is not probable.

I am indebted to Mr. C. B. Farrington for the analyses of the silver residues from the Soxhlet extractor.

5. Platinum Sesquioxide (Pt_2O_3) *and Hydroxide* (Pt_2O_3, $2H_2O$).—Platinum is rapidly attacked by fused sodium dioxide. In a spongy or finely-divided state and intimately mixed with sodium dioxide, platinum burns almost like tinder when heated to redness. If the combustion be started in a portion of the mixture it is transmitted rapidly throughout the mass, which becomes heated to bright redness. A platinum crucible withstands very few fusions of sodium dioxide.

Platinum sponge was fused with sodium dioxide in a platinum capsule until the mass became tranquil. The fusion-product was treated with water and a platinum compound of yellowish or muddy-green color remained undissolved. It settled slowly and was so finely divided as to render filtering impossible. It was washed several times by decantation and the remaining alkali was carefully neutralized with acetic acid. When neutral, the compound became yellow or very light brownish-yellow, resembling precipitated stannic sulphide in color. When the alkali was neutralized with carbon dioxide, or even when the compound was simply washed with distilled water until all of the alkali was removed, the same
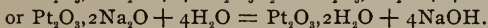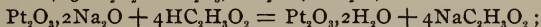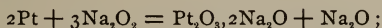
color change was produced. The yellowish-green compound is doubtless a very unstable sodium salt of the yellow hydroxide which is obtained on neutralizing, or on washing out, the alkali. Therefore the hydroxide has slightly acid properties.

The compound, after neutralizing the alkali, was washed by decantation until nearly pure, since it was not practicable to filter it, owing to its fine state of division. It was then dried over calcium chloride, thrown on a filter, washed a few times with dilute sulphuric acid, and finally with distilled water. Thus the alkali was all removed and the mass was again dried over calcium chloride.

Analysis proved the compound to have the formula Pt_2O_3, $2H_2O$, as shown below :

	Calculated for $Pt_2O_3,2H_2O$.	Found.	
		I.	II.
Pt	82.23	82.21	81.99
O	10.15	10.20	10.36
H_2O	7.62	7.59	7.65

The water was determined by direct weighing in a calcium chloride tube, the platinum by weighing the residue after heating to redness, and the oxygen by difference. The following reactions may represent the formation of the hydroxide :

$$2Pt + 3Na_2O_2 = Pt_2O_3,2Na_2O + Na_2O ;$$
$$Pt_2O_3,2Na_2O + 4HC_2H_3O_2 = Pt_2O_3,2H_2O + 4NaC_2H_3O_2 ;$$
or $Pt_2O_3,2Na_2O + 4H_2O = Pt_2O_3,2H_2O + 4NaOH.$

$Pt_2O_3,2H_2O$ is insoluble in alkalies, but it is reduced to platinum black on boiling with sodium hydroxide and alcohol. With acid the reduction does not take place. It is insoluble in nitric and sulphuric acids, also in cold dilute hydrochloric acid. Hot concentrated hydrochloric acid dissolves it slowly in the presence of air, forming platinic chloride. It dissolves slowly in aqua regia. The other hydroxides of platinum are readily soluble in acids. It is apparently unchanged on fusing with sodium hydroxide. It is reduced to platinum with incandescence on warming slightly in a current of hydrogen or coal gas. It does not lose water

at 100° C., but at 385° it loses 5.22 per cent, and at about 450° it is changed to Pt$_2$O$_3$. On heating to redness it is reduced to metallic platinum.

Platinum sesquioxide is a dark-brown, amorphous powder. It is insoluble in nitric, sulphuric, and hydrochloric acids, but dissolves slowly in concentrated hydrochloric acid in contact with air, forming platinic chloride. No salts corresponding to this oxide have been obtained.

The isolation of platinum sesquioxide fills a gap in the list of oxides of platinum which brings it into conformity with the other metals of this group, since osmium sesquioxide and iridium sesquioxide have long been known, as well as the sesquioxides of ruthenium and rhodium, palladium now being the only metal in the eighth group which has had no sesquioxides described. The corresponding sulphide of platinum, Pt$_2$S$_3$, has been described by Schneider.[1]

VANDERBILT UNIVERSITY,
  May 15, 1902.

XXXVIII.—ON THE SPECIFIC HEATS AND HEAT OF VAPORIZATION OF THE PARAFFIN AND METHYLENE HYDROCARBONS.

BY CHARLES F. MABERY AND ALBERT H. GOLDSTEIN.

Since 1819, when Dulong and Petit, on the basis of their work on thirteen of the chemical elements, announced the law that atoms of all elementary bodies possess the same capacity for heat, or that the specific heats of the elements vary inversely as their atomic weights, the specific heats of the elements have been important physical constants. With some exceptions, the constant 6.54 represents the product of the atomic weight into the specific heat. Later work showed that this law could be extended to compounds. In 1831, Neumann discovered that compounds with analogous composition have the same specific heat. Or in a series of compounds with analogous composition the specific heat varies inversely as the molecular weight. These laws apply to approximately 40 elements, and to solids only much below

[1] Pogg. Ann., **136**, 105.

their melting-points. The specific heats of many organic compounds have since been determined, and although no law has been stated, it is evident that, in certain homologous series of organic compounds, a condition exists in some of these series analogous to the law of Neumann. For instance, determinations have been made on a few of the alcohols with the following results :

Ethyl alcohol	0.680
Isopropyl alcohol	0.5286
Isobutyl "	0.5078
Isoamyl "	0.4932

That the variations on certain homologous series, so far as they have been observed, do not conform to a general law is shown by the following series, in which the specific heats increase with increase in molecular weights :

Methyl dichloracetate	0.3202
Ethyl dichloracetate	0.3384
Propyl dichloracetate	0.3506

In general, the data on specific heats of organic compounds are meager and not concordant. For the same substance the results of different observers seldom agree in the third decimal place ; they often do not agree in the second, and even in the first place (see tables of Landolt and Börnstein). These variations are probably due to the fact that specific heat is materially affected by impurities in the substance and the temperatures at which it is taken. Then, furthermore, the details of the determinations demand very careful attention to insure concordant results. In the determinations of the hydrocarbons to be described in this paper, it was found that impurities depressed the specific heats very considerably.

Although the paraffin series of hydrocarbons offers the best field for study of an homologous series, very little has been done in the direction of ascertaining the specific heats of these bodies. In a study of distillates separated from Pennsylvania petroleum, by Bartoli and Stracciati,[1] the specific heats of the following hydrocarbons were determined :

[1] Gazz. chim. ital., **15**, 417.

Hexane	C_6H_{14}	0.5042	$16°-37°$
Heptane	C_7H_{16}	0.4869	$16°-37°$
Octane	C_8H_{18}	0.5111	$12°-19°$
Decane	$C_{10}H_{22}$	0.5057	$14°-18°$
Tetradecane	$C_{14}H_{30}$	0.4995	
Hexadecane	$C_{16}H_{34}$	0.4963	$15°-22°$

The inference derived from these results was that the specific heats of these hydrocarbons were remarkably constant.

No data could be found relating to the specific heats of the methylene hydrocarbons C_nH_{2n}, nor those of the series still poorer in hydrogen. With the greatly extended uses of crude petroleum and refined distillates for fuel, in gasoline and oil engines, accurate information concerning specific heat and heat of vaporization is greatly desired.

Having in hand a great variety of hydrocarbons of the various series, which have been prepared in as pure form as possible, and numerous inquiries having been received for more complete information concerning these physical properties, it seemed advisable to make some determinations of these constants.

The hydrocarbons of the series C_nH_{2n+2} were obtained from Pennsylvania petroleum, those of the other series from California petroleum. Each hydrocarbon had been separated by a long process of distillation, and purified by treatment with sulphuric acid, sodium hydrate, and drying over sodium.

The determinations were made in a Bunsen ice calorimeter, to which was attached a capillary side-tube 70 cm. long, and the bore of such size that 1 cm. contained 0.0579 gram of mercury. To maintain the temperature at 0° the calorimeter was placed in a jar of ice-water with an excess of ice, and this jar was placed in another jar and the space between filled with cotton. The calorimeter was filled with air-free water and dry mercury, and the inside film of ice, 2 to 3 mm. thick, was formed by evaporation of ether by an air-blast within the inner tube. Approximately 2 grams of the hydrocarbon were placed in a small glass-stoppered tube of thin glass, whose heat equivalent was determined. The tube and hydrocarbon were heated to 50° in a larger tube placed in a beaker of water, kept at this temperature for at least fifteen minutes,

then transferred by a thread to the calorimeter. With care this could be done without loss of heat by radiation. The contraction of the mercury column was from 15 to 25 cm.

This method can be used for the paraffin hydrocarbons from C_6H_{14} to $C_{16}H_{34}$, the limit at which the hydrocarbons remain wholly liquid at 0°.

After obtaining the water constant of the apparatus, three to six determinations of each hydrocarbon were made at the temperatures 0° and 50°, with results given in the following table :

	Boiling-points.	Specific heat.
C_6H_{14}	68°	0.5272
C_7H_{16}	91°	0.5005
C_7H_{16}	98°	0.5074
C_8H_{18}	125°	0.5052
C_9H_{20}	151°	0.5034
$C_{10}H_{22}$	162°	0.4951
$C_{10}H_{22}$	172°	0.5021
$C_{11}H_{24}$	195°	0.5013
$C_{12}H_{26}$	214°	0.4997
$C_{13}H_{28}$	226°	0.4986
$C_{14}H_{30}$	242°	0.4973
$C_{15}H_{32}$	260°	0.4966
$C_{16}H_{34}$	275°	0.4957
Commercial gasoline		0.5135
Crude Ohio petroleum		0.4951

The following table gives the specific heats obtained from the series of methylene hydrocarbons :

	Boiling-points.	Specific heat.
C_6H_{12}	68°	0.5062
C_7H_{14}	98°	0.4879
C_8H_{16}	119°	0.4863
C_9H_{18}	135°	0.4851
$C_{10}H_{20}$	160°	0.4692
$C_{11}H_{22}$	190°	0.4819
$C_{12}H_{24}$	212°	0.4570
$C_{13}H_{26}$	232°	0.4573
$C_{14}H_{28}$	244°	0.4531
$C_{15}H_{30}$	263°	0.4708

It appears from these results that there is a uniform decrease in specific heat with increase in molecular weight. Furthermore, the normal hydrocarbons, such as heptane,

C_7H_{16} (b. p. 98°), and decane, $C_{10}H_{22}$ (b. p. 172°), have higher specific heats than their isomers, such, for example, as isoheptane, C_7H_{16} (b. p. 91°), and isodecane, $C_{10}H_{22}$ (b. p. 162°).

The same variation also appears in the methylene series, with high values for certain members that probably indicate different structural relations.

It is further interesting to observe the materially lower values given by the methylene hydrocarbons as compared with the values for the paraffin hydrocarbons. Whether this be due to greater compactness in the methylene molecule or to some quality of its ring structure, it would be interesting to ascertain.

Perhaps the falling off in specific heat with increasing molecular weight will appear to better advantage when arranged as ordinates on a curve with the molecular weights as abscissae. Only those compounds are given on the curve that are known to be normal, although, of course, this is not known with reference to the higher members. The different values of the isomers heptane and decane are shown on the shorter curve.

This uniform decrease in specific heat with increasing molecular weight in the series C_nH_{2n+2} suggests a constant relation analogous to the law of Neumann.

If the constant K be expressed in terms of the specific heat multiplied by the molecular weight and the product divided by the number of atoms in the molecule, the specific heats found for the hydrocarbons of this series give the following values for the constant :

Hydrocarbon.	Molecular weight.	Specific heat.	No. of atoms.	K.
C_6H_{14}	86	0.5272	20	2.26
C_7H_{16}	100	0.5074	23	2.21
C_8H_{18}	114	0.5052	26	2.21
C_9H_{20}	128	0.5034	29	2.22
$C_{10}H_{22}$	142	0.5021	32	2.23
$C_{11}H_{24}$	156	0.5013	35	2.23
$C_{12}H_{26}$	170	0.4997	38	2.23
$C_{13}H_{28}$	184	0.4986	41	2.24
$C_{14}H_{30}$	196	0.4973	44	2.23
$C_{15}H_{32}$	210	0.4966	47	2.24
$C_{16}H_{34}$	224	0.4957	50	2.23

The constant, therefore, for the homologous series of hydrocarbons C_nH_{2n+2} is 2.23.

A similar curve drawn for the specific heats of the methylene hydrocarbons, so far as they were determined, show also a regular variation.

The constant K, for the methylene hydrocarbons, calculated from the determinations, shows a somewhat higher mean value than that of the paraffin hydrocarbons:

Hydrocarbon.	Molecular weight.	Specific heat.	No. of atoms.	K.
C_6H_{12}	84	0.5062	18	2.26
C_7H_{14}	98	0.4879	21	2.28
C_8H_{16}	112	0.4863	24	2.37
C_9H_{18}	126	0.4851	27	2.27
$C_{11}H_{22}$	154	0.4819	33	2.25
$C_{15}H_{30}$	210	0.4708	45	2.20

The values for the specific heats of both hexane and hexamethylene are higher than should be expected from the results on the other members of the series. These hydrocarbons were well purified, except it seems probable that the distillates contained certain proportions of both.

Determinations were also made of the specific heats of a series of hydrocarbons separated from the high-boiling portions of Pennsylvania petroleum. This series is under examination to establish its composition and relations to series separated from heavy petroleums from other fields. These hydrocarbons were cooled to —10°, and filtered to remove so far as possible the solid hydrocarbons with which they are associated in Pennsylvania petroleum. They have been shown to be members of the series C_nH_{2n}. A more detailed description of these bodies will be presented in a subsequent paper, which is now in preparation.

The following values were obtained for the specific heats of these hydrocarbons:

	Boiling-point.	Specific heat.
$C_{16}H_{32}$	173°	0.4723
$C_{18}H_{36}$	202°	0.4723
$C_{20}H_{40}$	223°	0.4706
$C_{23}H_{46}$	260°	0.4612
$C_{24}H_{48}$	272°	0.4586

From data obtained with the paraffin hydrocarbons, there is no opportunity to compare the specific heats, although the sudden drop from the last member examined of the series C_nH_{2n+2}, $C_{16}H_{34}$ (specific heat 0.4957), to the first member of the last series above in which the solid hydrocarbon, $C_{16}H_{32}$ (specific heat 0.4723), had been removed by cooling and filtration, shows a marked difference in structure. This relation appears in the longer curve in the table.

Comparing the last member of the series C_nH_{2n} from California oil $C_{15}H_{30}$ (specific heat 0.4708), with the hydrocarbon $C_{16}H_{32}$ (specific heat 0.4746), it appears that the series C_nH_{2n} from Pennsylvania petroleum is a continuation of the same series from California petroleum. Unfortunately, the higher members of the series from California petroleum were not available for comparison. But results already obtained as to the composition, specific gravity, refractive index, etc., are in accord with the specific heats. The specific heat was also determined in several hydrocarbons of the series C_nH_{2n-2}, and the series C_nH_{2n-4}, which had been separated from Texas petroleum with the following results:

Series C_nH_{2n-2}.

	Boiling-point at 50 mm.	Specific heat.	K.
$C_{14}H_{26}$	$127°$	0.4447	2.15
$C_{15}H_{28}$	$142°$	0.4439	2.15
$C_{16}H_{30}$	$162°$	0.4426	2.14

Series C_nH_{2n-4}.

	Boiling-point at 50 mm.	Specific heat.
$C_{21}H_{38}$	$218°$	0.4560
$C_{25}H_{46}$	$273°$	0.4650

The latter results cannot be accepted as reliable, for the quantities of the hydrocarbons were very small, and the oils began to crystallize at 0°. There is no doubt that the specific heats of these hydrocarbons are smaller than those of the preceding series.

To convey a clear idea of the variation in hydrocarbons in the same series, and also to show the difference between the different series, the results are brought together on the following coordinate table:

$C_n H_{2n+2}$

$C_6 H_{12}$ $C_7 H_{16}$
$C_8 H_{18}$
$C_9 H_{20}$
$C_{10} H_{22}$
$C_7 H_{16} (iso)$ $C_{11} H_{24}$
$C_{12} H_{26}$
$C_{13} H_{28}$
$C_{14} H_{30}$
$C_{15} H_{32}$
$C_{16} H_{22} (iso)$ $C_{15} H_{44}$

$C_7 H_{16}$
$C_8 H_{16}$
$C_9 H_{18}$

$C_{11} H_{22}$

$C_n H_{2n}$ (PENNA)

$C_{16} H_{32}$
$C_{18} H_{36}$
$C_{15} H_{30} (?)$ $C_{20} H_{40}$

$C_{23} H_{46}$
$C_{24} H_{48}$

$C_n H_{2n-2}$ (TEXAS)

$C_{14} H_{26}$
$C_{15} H_{28}$
$C_{16} H_{30}$

.520
8
6
4
2
.510
8
6
4
2
500
8
6
4
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490
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6
4
2
480
8
6
4
2
470
8
6
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6
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8
6
4
2
440

80 100 120 140 160 180 200 220 240 260 280 300 320 340
Molecular Weight
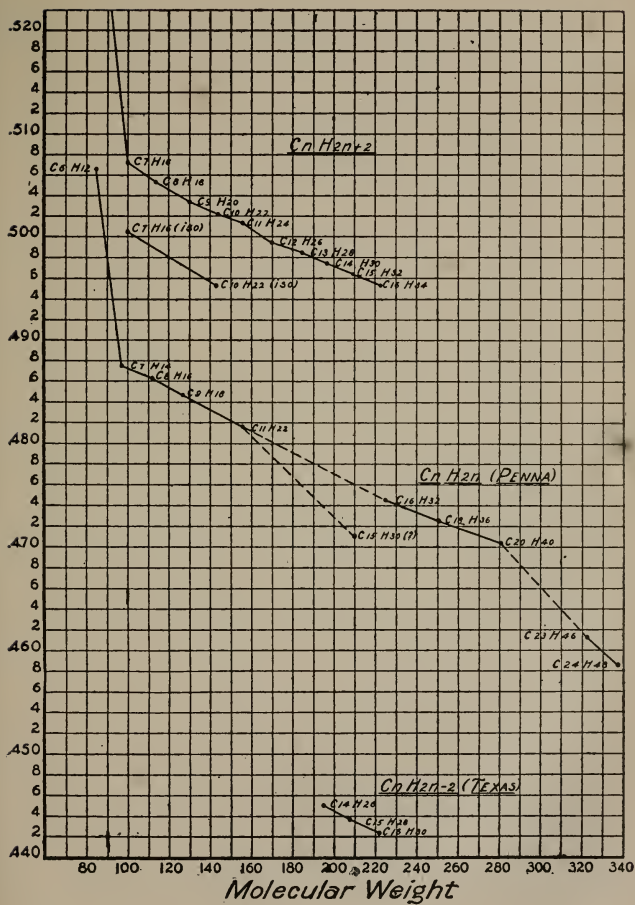
The regular variation in members of the series C_nH_{2n+2} appears in its curve, and the differences in what are known to be isomeric forms in the same series. It is further interesting to observe the continuation of the curve representing the members of the series C_nH_{2n} from the curve containing the members of the series C_nH_{2n} from California petroleum. The lower values in the series C_nH_{2n-2} from Texas petroleum form a characteristic curve near the base of the table.

The specific heat was determined in the following crude oils from various fields :

	Specific gravity.	Specific heat.
Pennsylvania	0.8095	0.5000
Berea grit	0.7939	0.4690
Japanese	0.8622	0.4532
Texas (Lucas well)	0.9200	0.4315
Russian	0.9079	0.4355
Wyoming	0.8816	0.4323
California	0.9600	0.3980
Texas	0.9466	0.4009
Ohio	. . . .	0.4951
Commercial gasoline	. . . .	0.5135

These values show that the specific heat of the crude oils is an important property from a practical point of view. It also appears that there is no close agreement between specific heat and specific gravity. Pennsylvania oil stands at the head, and Berea grit, with a much larger proportion of volatile constituents, is next. Of the heavier oils, it appears in general that the specific heats are much lower, but with no definite relation.

It would be interesting to ascertain the specific heats of the less volatile constituents of petroleum from different fields, including the solid hydrocarbons. This would require observations at different temperatures, and it would add to the interest of the data if all determinations could be made within a wide range of temperatures.

Heats of Vaporization of Hydrocarbons of the Paraffin and Methylene Series.

Since it had been found that a boiling-point constant can be calculated from the absolute boiling-point and latent heat of

evaporation, which may be used as a basis of a method for the determination of molecular weights, more complete knowledge of the latent heat of evaporation or heat of vaporization of liquids at their boiling-points has become of great importance. From a practical point of view, the greatly extended use of crude petroleum and its constituents can only be economically continued with the aid of further information concerning the heats of vaporization. Numerous inquiries from persons interested in these directions attest an appreciation of further knowledge on this subject.

In 1885 the following law was proposed by Dudley, on the heats of vaporization of members of a homologous series.[1]

" In any homologous series the heat of vaporization in a unit of volume of the vapor, under the same conditions of temperature and pressure, is proportional to the density and also to the absolute boiling-point." This generalization was based on data selected from determinations of the heats of vaporization of the formates, acetates, propionates, butyrates, isobutyrates, alcohols, and aromatic hydrocarbons.

With numerous members of the different series of hydrocarbons at hand, it was our intention to determine the latent heats of the series C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-2}. But the only apparatus available was constructed of glass, which would not withstand the high temperatures necessary in determinations of the hydrocarbons with high boiling-points, and the time was too limited to permit of the construction of a metallic apparatus.

For the apparatus used we are indebted to the kindness of Professor Kahlenberg, of the University of Wisconsin, who allowed us to use the form devised by him, before he had published his description, which appeared in the *Journal of Physical Chemistry*, **5,** 215 (1901).

This apparatus is an ingenious modification of Berthelot's method, in which the substance is heated and volatilized by means of an electric current within the body of the liquid, thus avoiding errors due to external heating. Through the kindness of Professor Kahlenberg and Professor Trevor we

[1] J. Am. Chem. Soc., **17,** 985.
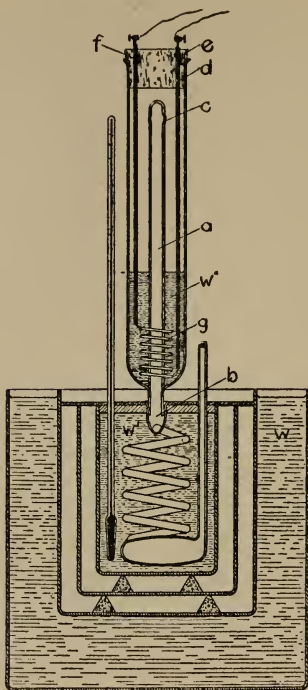
are able to show, in this connection, the form of this apparatus.

In the publication referred to, the apparatus is described as follows : '' The retort consists of a tube 17 cm. long and 5.5 cm. in diameter, into the bottom of which is fused a tube which fits into a condenser with a ground-glass joint. At the other end of the inner tube are two large lateral openings. Glass tubes pass through the cork at the top, and into these are fused the ends of the spiral of platinum wire. This spiral consists of about 40 cm. of fairly stout platinum wire, to the ends of which are welded short, heavy pieces of platinum rod,

and these rods are, in turn, fused into the glass tubes. Long, rather heavy copper wires pass down into the glass tubes, at the bottom of which they are connected with the ends of the platinum rods by means of a few drops of mercury. The calorimeter is covered with a heavy piece of asbestos board and the retort is enclosed in asbestos and cotton batting.''

A current of from 8 to 10 amperes, regulated by a rheostat, gave sufficient heat to vaporize from 20 to 30 grams of the oil in from five to six minutes. The calorimeter, about 2500 cc. capacity, was made of thin nickel-plated sheet copper. It was elliptical in form, to conform to the shape of the condenser, and was provided with a copper stirrer. The capacity of the calorimeter was reduced, as shown in the figure, by bending closer together the glass tubes leading from the body of the condenser. Temperatures were taken on a Beckmann thermometer.

The water equivalent of the calorimeter, condenser, stirrer, and thermometer were found to be 185 grams, practically the same value as the equivalent calculated from the weights and specific heats of the parts of the apparatus.

As mentioned above, this form of the apparatus is limited in this work by the fact that when oils of boiling-points higher than 125° are volatilized, the sudden change in temperature at the water line of the condenser is so great that glass will not stand it.

The following results were obtained with a few members of the series C_nH_{2n+2}, as the mean of several observations :

	Boiling-point.	Heat of vaporization in calories.
Hexane, C_6H_{14}	68°	79.4
Heptane, C_7H_{16}	98°	74.0
Octane, C_8H_{18}	125°	71.1

Determinations were also made on the methylene hydrocarbons that could be volatilized in this form of apparatus :

	Boiling-point.	Heat in calories.
Hexamethylene, C_6H_{12}	68°–70°	87.3
Dimethylpentamethylene, C_7H_{14}	90°–92°	81.0
Methylhexamethylene, C_7H_{14}	98°	75.7
Dimethylhexamethylene, C_8H_{16}	118°–119°	71.7

These results indicate a rapid falling off in latent heat, with increase in molecular weight. It is to be regretted that we had not the metallic condenser, which would have enabled us to carry these observations up to include the less volatile hydrocarbons of both series. Advantage will be taken of the earliest opportunity to continue this work.

The hydrocarbons used in the work described in this paper were prepared with assistance granted by the Academy from the C. M. Warren Fund for Chemical Research.

REPORT.

Algal Wax and Its Relationship to Petroleum.

It will be remembered that Kraemer and Spilker[1] published a new theory of the formation of petroleum, which assumed that the oil contained in diatoms was probably the raw material from which mineral wax, petroleum, and natural gas were derived by natural distillation. They obtained a considerable quantity of a recent diatomaceous deposit from which a wax-like substance was extracted by means of benzene. This, by distillation under pressure, yielded a liquid resembling crude petroleum, besides gaseous products, and a residue consisting of carbon and paraffin.

Engler,[2] in his reply to this article, calls attention to one by Stahl[3] which was not mentioned by Kraemer and Spilker. Stahl suggested essentially the same idea, except that he believed the deposits to have been formed in more or less enclosed arms of former seas, instead of in fresh-water lakes. Engler then calls attention to his own well-known suggestion that petroleum is derived from deposits of marine animals. The fat contained in them is first saponified by water, and finally changed to petroleum by pressure and heat, or possibly by pressure alone. Zaloziecki and others regarded mineral wax as an intermediate product, but Engler thinks the evidence is not sufficient to warrant such a conclusion. It is well known that mineral wax was distilled on a large scale to obtain petroleum and paraffin.

By the distillation of stearic and oleic acids and their glycerides, and of fish oil, Engler[4] obtained petroleum, and he showed later[5] that "all possible kinds of animal and vegeta-

1 Ber. d. chem. Ges., **32**, 2940 (1899); see also this JOURNAL, **23**, 176.
2 *Ibid.*, **33**, 7 (1900).
3 Chem. Ztg., (1889), p. 144.
4 Ber. d. chem. Ges., **21**, 1716; **22**, 592.
5 *Ibid.*, **30**, 2358.

ble fats and oils'' could be changed to petroleum. Hence it would have been surprising if Kraemer and Spilker had not obtained petroleum by distilling diatom fat, mineral wax, and Carnauba and Japan waxes. As all vegetable and animal fats yield practically the same products when distilled under pressure, this evidence is of no value in deciding between the two theories.

The comparison of the composition of the ash of the diatomaceous deposit and that of the oil-bearing rock is of no value, because, as Kraemer and Spilker acknowledge, the diatoms must have been buried under detritus from the surrounding hills. Even a closer agreement in their composition would have been of no value in deciding the question under discussion.

Kraemer and Spilker thought that the chief objection to Engler's theory was that it was not easy to account for the vast deposits of marine animals necessary to form the petroleum. Engler replied that by alternate rising and sinking of the shore, bays might be cut off from the sea and develop new fauna as the water became less salt. These animals would be killed when the shore sank and the salt water was readmitted. Deposits of animal remains might also be formed by fresh water killing marine species, or by the over-production of animal life owing to the lack of carnivora. Also diseases, or earthquakes, or submarine volcanic activity may be mentioned. But above all is the action of currents that carry animal remains into bays or other sheltered places. It is probable that the microscopic animals play a far greater part than the larger ones.

It is well known that the Globigerina ooze covering the bottom of the Atlantic ocean, and other similar deposits, are largely composed of the remains of minute animals. Also the plankton, the floating fauna, composed mainly of animals without calcareous or siliceous organs, contributes very largely to the formation of bitumen.

Of great interest are the observations made by Andrussow and Lang in the Black and Caspian seas. The Adschidarja, a bay having an area of 15,500 sq. km., that is, as large as Saxony, is connected with the Caspian by a channel 100 to 500 meters wide. Owing to a difference in level, there is always a current flowing at the rate of 64 meters a minute into this bay. The water in the bay has the density 17° Bé., while that of the sea is 0°.5 to 1° Bé., so that all animals carried in by the current are killed and their bodies are deposited in great beds. Great numbers of fish also pass through the canal during the spawning season and die when they reach

the bay. These animal remains are more or less mingled with sand and dust carried into the bay by violent winds from the surrounding steppes. In time the bay will be completely filled in. The occurrence of fish remains, in connection with bitumen and petroleum deposits, is an important indication.

It was noticed by the Russian deep-sea expedition that, in parts of the Black Sea where the water is undisturbed by currents, there is so much hydrogen sulphide in solution that no animals can live, and there are large deposits of animal remains slowly decaying. Andrussow believes that the Black Sea and the Mediterranean bear the same relation to one another, as the Caspian Sea and Adschidarja. In the Red Sea, also, we find a somewhat similar state of affairs combined with an overproduction of animal life. The masses of tarry substance, and the oily surface often seen there, go to prove the truth of this theory.

The deposits of petroleum at Baku and the surrounding regions are nearly all tertiary. During that period there was an immense sea which became shallower as the land rose, and the Aral and Caspian seas, and other bodies of water, were cut off. It is certain that the menilite slate in which the petroleum occurs is of marine origin. Szajnocha laid stress on the fish remains found in this slate. He estimated that if the annual deposition of fish equaled the production of the fisheries in the northern waters of Europe, and the oil from these yielded only 50 per cent of petroleum, a period of only 2,560 years would have sufficed to produce the entire Carpathian petroleum deposit. Such a period is but a geological day.

In one or two fossil beds there have been found ammonites and mussels, with the shells filled with petroleum.

Engler does not deny that diatoms and other plants may yield petroleum, but regards it as very improbable that the larger petroleum deposits were formed from diatoms. The invariable presence of salt and brine indicates marine origin, as does also the geological evidence. For that reason Stahl's theory is preferable to that of Kraemer and Spilker. Höfer showed that the petroleum deposits have no connection with beds of turf, lignite, or coal, which are of fresh water origin.

The decay of the diatoms would yield at most 0.05 to 0.1 per cent of ammonium carbonate, so that it is very unlikely that their siliceous coverings would be dissolved, as suggested by Kraemer and Spilker.

It is not safe to say that the bitumen of peat-bogs is derived from diatoms, for Guignet and Durin have shown that the

wax extracted from peat by solvents closely resembles that obtained from living moss and other plants.

Quite recently Kraemer and Spilker[1] have published a modification of their theory. By extracting various kinds of peat, turf, and pyropissite with hot benzene or toluene, they came to the conclusion that the amount of wax is independent of the number of diatoms found in the material extracted. It is their belief that many other kinds of algæ besides diatoms have contributed to the wax, as it has been shown that oil drops are contained in the cells of the *Ulothrichaceæ*, *Phyllosiphoniaceæ*, and the *Vaucheriaceæ*. In the course of thousands of years everything but the oil would decay. Animal fats very soon become rancid.

When distilled under atmospheric pressure the crude wax yielded the same products as when distilled under considerable pressure. With reduced pressures, however, a wax-like distillate was obtained, while an asphalt-like mass, containing coke and sulphur, remained in the retort. The wax, when redistilled, came over unchanged. When first heated under reduced pressure, the crude wax yielded carbon monoxide and dioxide, hydrogen sulphide, and water with an acid reaction. If further heated under atmospheric pressure, methane, olefines, and carbon dioxide escape, while a semi-liquid mass of petroleum hydrocarbons passes over. The water smells of acetic acid and its volatile homologues. It is, therefore, probable that the crude wax contains easily decomposed substances, besides a mixture of a monacid ester mixed with free acid. This was shown by determining the acid number and saponification number of different specimens of wax. By saponification an acid approximating arachidic, behenic, and lignoceric acids in composition and melting-point was obtained. It was probably a mixture of all three acids, possibly with higher homologues. The alcohol set free contained 20 to 22 carbon atoms, and was probably a mixture also. No traces of glycerides were found.

These esters would easily yield methane, carbon dioxide, paraffins, and olefines when distilled under pressure. Naphthenes would be produced by ring formation. Hence the differences noted in various kinds of petroleum are not to be explained by differences in the raw materials, but are caused by dynamic agencies,—pressure and heat.

The presence of sulphur, and of organic sulphides formed from it, is due to sulphur bacteria.

Mineral wax is an important product intermediate between algal wax and petroleum. They were able to show that it

[1] Ber. d. chem. Ges., **35**, 1212 (1902).

contains small quantities of an ester. It also contains sulphur and resin, and yields water, volatile fatty acids, and carbon dioxide when distilled, all of which shows its relationship to algal wax. The ash of mineral wax was shown to be similar in composition to that of a recent diatomaceous deposit.

Animal remains may have occasionally formed some petroleum, but the presence of sulphur and the rare occurrence of nitrogen compounds stand in the way of Engler's theory. Calculations are given to prove the possibility of the formation of the vast deposits of wax and oil from algæ.

It seems to the reviewer that very little has been added by the last paper. As pointed out by Engler, it is not improbable that petroleum may be of both animal and vegetable origin, and it is for the geologist to decide in any given case.

C. E. WATERS.

OBITUARY.

The *Berichte* of May 10th contains a brief notice of the death of Professor von Pechmann, of Tübingen, on April 19th. In October last an illness so affected his mind that he was compelled to spend the winter in a sanatorium for nervous diseases. He seemingly recovered, and at the beginning of this summer-semester returned to his work, but broke down again, and in an acute attack of melancholia, swallowed prussic acid.

Freiherr Hans von Pechmann was of a distinguished Munich family. He was a pupil of von Baeyer, at Munich, where he took the Ph.D. degree, and became Privatdocent. In 1884 he was given the chair of analytical chemistry, in Munich, made vacant by the death of Clemens Zimmermann. In 1895 he accepted a call to the full professorship in Tübingen.

Von Pechmann was of a very genial disposition, a delightful companion and friend, and an indefatigable worker in the field of organic chemistry. His fellow-student and friend, Professor Königs, of Munich, is to write an article on his investigations for the *Berichte*.   E. R.

AMERICAN

Chemical Journal

REACTIONS BETWEEN ACID AND BASIC AMIDES
IN LIQUID AMMONIA.

By Edward C. Franklin and Orin F. Stafford.

The close analogy existing between liquid ammonia and
water as electrolytic solvents has been shown in some recent
papers by Franklin and Kraus.[1]   Among other points of anal-
ogy these authors call attention to the fact that acid and basic
amides bear a relation to liquid ammonia which in many re-
spects is very similar to that borne by ordinary acids and
bases to water.   Conductivity measurements, for example,
have shown that ammonia solutions of acid and basic amides
are conductors of electricity, a fact due presumably, since
ammonia itself has a conductivity of the same order as that of
water,[2] to the dissociation of the basic amides into metal cation
and amide anion,

$$MeNH_2 \; \rightleftharpoons \; Me^{\cdot} + NH'_2,$$

and a similar dissociation of the acid amide into acid anion

[1] This Journal, **20**, 820 (1898) ; **20**, 836 (1898) ; **21**, 1 (1899) ; **21**, 9 (1899) ; **23**, 277
(1900).

[2] Franklin and Kraus : *Ibid.*, **23**, 285 (1900) ; Frenzel : Ztschr. Elektrochemie,
6, 479 (1900).

and hydrogen ion, or, more probably, hydrogen associated with ammonia as ion, as indicated herewith,

$$AcNH_2 \rightleftarrows AcNH' + H^. \text{ or } H(NH_3)_n^..$$
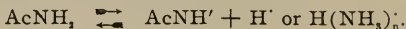
Further, since the acid amides contain two amide hydrogen atoms, it is probable that equilibrium also exists between the anion $AcNH'$ and its dissociation-products as indicated in the equation

$$AcNH' \rightleftarrows Ac'' + H^. \text{ or } H(NH_3)_n^..$$
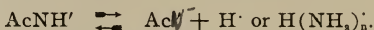
This view of the acid and basic characters of the amides in question would seem to be further substantiated by their power, when in ammonia solution, to bring about many of the identical color changes that are characteristic of the well-known indicators used in acidimetry and alkalimetry.[1]

These considerations, taken together with the facts developed in the papers above mentioned bearing upon the close similarity existing between water and ammonia as solvents, make it highly probable that in ammonia solutions reactions should occur between acid and basic amides with all the facility that marks the interaction of ordinary acids and bases in water. At the risk of being unnecessarily explicit, the following parallel reactions are given for the potassium hydroxide-acetic-acid-water system and the analogous potassium-amide-acetamide-ammonia system :

$K^. + OH' + CH_3COO' + H^. = CH_3COO' + K^. + H_2O$;
$K' + NH'_2 + CH_3CONH' + H^. = CH_3CONH' + K^. + NH_3$;
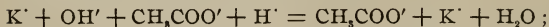
and since there is a second amide hydrogen atom in the acid amide, another reaction is theoretically possible in the ammonia system,

$$K^. + NH'_2 + CH_3CON'' + H^. + K^. =$$
$$CH_3CON'' + 2K^. + NH_3.$$
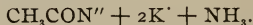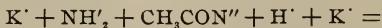
These reactions, written in the ordinary molecular formulæ, are :

$$KOH + CH_3COOH = CH_3COOK + H_2O ;$$
$$KNH_2 + CH_3CONH_2 = CH_3CONHK + NH_3 ;$$
$$2KNH_2 + CH_3CONH_2 = CH_3CONK_2 + 2NH_3.$$
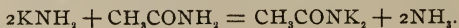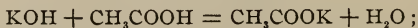
[1] *Loc. cit.*

The substances formed in this way should, in all probability, be salt-like bodies appearing as precipitates in case they are insoluble, or in case they are soluble, allowing themselves to be crystallized from their solutions.

As a matter of fact, many compounds of the kind in question have been prepared and are described in the literature,[1] but by one investigator only have any of them been made by the interaction of acid and basic amides. Titherly[2] has obtained the sodium derivatives of formamide, acetamide, propionamide, and benzamide as amorphous precipitates by the continued action of hot benzene solutions of the acid amides upon sodium amide. Some qualitative experiments by Franklin and Kraus[3] show that compounds of this class are formed with marked facility when the acid and basic amides are brought together in ammonia solution.

Theoretically, then, it would seem that the possibilities for the formation of new compound in the ammonia system would be limited only by the number of available acid and basic amides. There is a corresponding acid amide for nearly every one of the known oxygen acids, and when to this class of compounds are added the nitrides of the non-metallic elements and the whole list of ammonium salts, which have been shown to be analogous in some respects, when in ammonia solution, to the oxygen acids in water, the number of substances that might be expected to act as acids is very great. On the other hand, the number of substances capable of acting as bases is somewhat limited. Many metallic nitrides have been prepared, but the number of known basic amides is small. Of the metallic amides analogous to the hydroxides only those of sodium,[4] potassium,[4] lithium,[5] calcium,[6] and zinc[7] have been

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[1] Dessaignes : Ann. Chem. (Liebig), **82**,*231 (1852) ; Frankland : Jsb., 1857, p. 419; Strecker : Ann. Chem. (Liebig), **103**, 324 (1857) ; Landsberg : *Ibid.*, **215**, 172 (1882) ; Gal : Bull. soc. chim., **39**, 647 (1883) ; Curtius : Ber. d. chem. Ges., **23**, 3037 (1891) ; Blacher : *Ibid.*, **28**, 432 and 2352 (1895) ; Titherly : J. Chem. Soc. (London), **71**, 461 (1897).

[2] *Loc. cit.*

[3] *Loc. cit.*

[4] Gay Lussac and Thenard : Watts' Dict., Vol. IV., pp. 299 and 475 (1894) ; Beilstein and Geuther : Ann. Chem. (Liebig), **108**, 88 (1858); Baumer and Landolt : Ann. Chem. (Liebig), **111**, 1 (1859); Joannis : Compt. rend., **112**, 392 (1891).

[5] Titherly : J. Chem. Soc. (London), **65**, 504 (1894).

[6] Moissan : Bull. soc. chim., [3], **21**, 909 (1899).

[7] Frankland : *Loc. cit.*

described, though the fact that solutions of potassium amide give precipitates in ammonia solution[1] with the salts of many of the heavier metals makes it probable that by this method a considerable number of new amides may be prepared.

Hence it appears that the theoretical possibilities for salt formation in the ammonia system might be expected to approach in extent that of the water system. It has therefore seemed worth while to study the products of the interaction of one or two typical basic amides with several of the available acid amides, to confirm, if possible, the theoretical considerations just advanced.

Method of Preparation.

An idea of the method used in making most of the substances described in this paper can be obtained from the following account of the preparation of a potassium compound. A weighed quantity of metallic potassium is introduced into the preparation tube (Fig. I.), which has previously been filled to about the point a with liquid ammonia. The metal dissolves at once, forming a characteristic blue solution.[2] Upon allowing the preparation to stand, the blue color gradually disappears with the evolution of hydrogen gas. This decolorizing process, which marks the gradual change of potassium-ammonium into potassium amide, requires several hours. It is usually desirable, therefore, to seal the tube at β, withdraw it from the bath of liquid ammonia, in which it is necessary to keep it while open, and allow it to stand at laboratory temperature until needed. In case the quantity of metal introduced is large, it has been found advisable to open the tube occasionally to permit the accumulated hydrogen to

[1] For example, when a solution of potassium amide is added to a solution of nickel nitrate a chocolate-colored precipitate is formed. Lead nitrate or lead iodide gives a yellow precipitate, calcium nitrate and zinc nitrate give white precipitates, while with copper nitrate and magnesium nitrates no precipitates are produced. When potassium amide solution is added to a solution of silver nitrate or iodide a white precipitate is formed which, when dry, is exceedingly explosive. A number of attempts to determine the atomic ratio between the silver and nitrogen in this compound indicate the probable formation of silver amide. The results of the study of these reactions will be given in a future paper.

[2] This blue liquid behaves in most respects like a simple solution of metallic potassium in liquid ammonia. According to Joannis (Compt. rend., **115**, 820 (1898)) the solution contains the compound $KNH_2—NH_3K$, which he calls potassammonium.
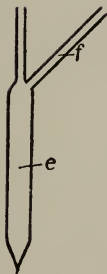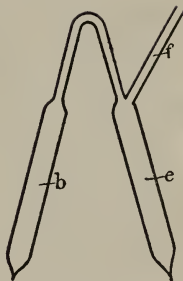
Fig. I.   Fig. II.   Fig. III.

escape. The resulting solution of potassium amide is a clear, mobile liquid, generally of a light-yellow color. Usually there is mixed with it more or less potassium hydroxide in the form of an amorphous, insoluble mass, the reaction-product, doubtless, of moisture that in various ways might enter the tube during the introduction of the materials used. By careful decantation of the liquid into the other end of the tube, however, the precipitate may be retained in the arm *a*, with which it is subsequently removed, the tube being cut at *d* for this purpose after taking the precautions—always necessary in opening and closing tubes containing liquid ammonia

—to cool the contents in a bath of liquid ammonia and to in-
sure the absence of all internal pressure by opening the capil-
lary at *c.* In place of the part removed is sealed the recepta-
cle shown in Fig. II., after which the apparatus is bent into
the form shown in Fig. III., the two arms being left divergent
to facilitate the transference of liquid from one arm to the
other. With the arm *b* still immersed in liquid ammonia, a
weighed quantity of the acid amide is introduced into the arm
e through the tubulure *f.* In case the apparatus contains an
insufficient quantity of liquid for the operations to follow, *e* is
immersed in a cooling-bath and the requisite quantity of am-
monia is introduced through *f* from a pipette. The tubulure
is then closed before the blowpipe, care being taken to avoid
contamination of the contents of the apparatus with moisture
from the flame. In case no ammonia has been placed directly
upon the acid amide by introduction through *f* as just de-
scribed, the arm *e* of the sealed apparatus is placed in a cool-
ing-bath—most frequently in these experiments liquid ammo-
nia itself—whereupon the solvent rapidly distils over from *b*
and immediately dissolves the amide. The tube is then per-
mitted to warm up to the temperature of the laboratory. If
now either solution be poured into the other the results of the
reaction can be observed. In case a precipitate is produced
the mother-liquor is poured therefrom into the empty arm of
the tube and pure ammonia is distilled from this mother-
liquor back upon the solid substance. This ammonia, after
agitation with the precipitate, is again poured back into the
other arm of the apparatus. This operation is repeated as
often as may be considered desirable. The arm of the tube
containing the washed substance is at last sealed off to a long
capillary point through which the vapor of the solvent may
escape slowly, and so prevent the violent boiling and bump-
ing—entailing always the risk of mechanical loss of ma-
terial—that usually accompanies the evaporation of liquid
ammonia from open narrow tubes. As soon as the last traces
of liquid disappear the tube is sealed and preserved until its
contents are needed for further examination.

The object in view in undertaking this investigation was to

demonstrate the existence of certain compounds rather than to make any detailed study of their properties. The work, therefore, has been confined almost entirely to the preparation and analysis of the substances to be described, although incidentally some properties were observed. In general, it may be said that the compounds are easily soluble in water, in which they suffer more or less complete hydrolysis. The amides used, both basic and acid, are easily soluble in liquid ammonia, though the products of their interaction present the greatest diversity of solubility in that medium. Some of the potassium compounds, for example, are apparently insoluble, others so very soluble that a separation of the solid substances from the mother-liquors is impossible, while between these two extremes are compounds the solubility of which permits their ready recrystallization.

Methods of Analysis.

The difficulties encountered in the analytical part of the work were not inconsiderable. The intensely hygroscopic character of the compounds, indeed, has rendered the questions of proper desiccation and accurate weighing among the most serious problems in the research. Many of the compounds stand heating, without apparent decomposition, to 100° in the double-tube arrangement shown in Fig. IV., in which
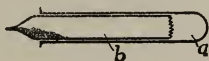
Fig. IV.

b is the opened preparation-tube and a a snugly fitting test-tube. This treatment generally drives off the adherent ammonia completely, while the diffusion of water vapor into the apparatus from the atmosphere is negligible. In some cases, however, especially in the presence of traces of moisture, incipient decomposition is produced which is itself productive of ammonia. The dividing line between these two kinds of ammonia is sometimes exceedingly hard to locate, a fact that has done much to render certain of the analytical

results less concordant than is desirable, though it is thought that in none of the cases given below are the discrepancies great enough to bring the identity of the compounds into question.

Nitrogen was determined partly by the absolute method of Dumas and partly by the Kjeldahl method. In using the latter the hydrolysis of the compound was insured by treating it with hot sulphuric acid, after which the solution was made alkaline, and the ammonia distilled by the aid of a current of steam into standard acid.

Potassium was determined by igniting the salt and subsequently converting the residue into the sulphate according to the directions of Fresenius.

Magnesium was weighed as magnesium pyrophosphate. The salt was hydrolyzed by treatment with hydrochloric acid after which the usual procedure, as described by Fresenius, was followed.

Sulphur was converted into the sulphate ion and weighed as barium sulphate, according to the method of Carius.

Potassium Salts.

The greater number of compounds described in this paper have been made by the action of potassium amide on the respective acid amides. The reasons which have led us to study especially the potassium salts are the much greater solubility of potassium amide over that of the other known metallic amides and the greater ease with which this basic amide is formed by the interaction of the metal and liquid ammonia. A quantity of potassium-ammonium contained in one of the above-described preparation-tubes is usually completely decomposed after a few hours at laboratory temperature, while the decomposition of sodium-ammonium or lithium-ammonium is complete only after the lapse of many days. In the case of several tubes containing sodammonium, the transformation into sodium amide was not finished even after standing for six months. Potassium amide is very soluble in liquid ammonia. It separates from very concentrated solutions as a colorless, well-crystallized, highly hygroscopic mass. Beautiful crystals are formed when the solution is

carefully evaporated. Joannis[1] has shown that the action of ammonia on the ammonia solution of metallic potassium is represented by the equation

$$K + NH_3 = KNH_2 + H,$$
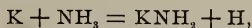
and while it is probably unnecessary for the identification of the compound we have, nevertheless, made determinations of the potassium in two specimens of the substance, as follows :

I. 0.1250 gram substance gave 0.1654 gram KCl.
II. 0.1198 gram substance gave 0.1626 gram KCl.

	Calculated for KNH_2.	I.	Found.	II.
K	70.90	69.44		71.10

Monopotassium Acetamide, $CH_3CONHK.nNH_3$. — When equimolecular quantities of potassium amide and acetamide are brought together in the apparatus described above and the solution is cooled in a bath of liquid ammonia, colorless crystals of monopotassium acetamide separate from the concentrated solution. Since the substance is very soluble in ammonia it was not possible to wash the crop of crystals. The product was therefore simply drained of mother-liquor, dried at laboratory temperature, and submitted to analysis with the following results :

I. 0.1628 gram salt gave 0.1380 gram K_2SO_4.
II. 0.3500 gram salt gave 0.0499 gram N.
III. 0.1357 gram salt gave 0.1184 gram K_2SO_4.

	Calculated for CH_3CONHK.	I.	Found. II.	III.
K	40.21	38.09	....	39.21
N	14.44	....	14.26	....

The same substance is also formed by the action of metallic potassium on a solution of acetamide. The action is very vigorous and is accompanied by the evolution of hydrogen gas. Monopotassium acetamide contains ammonia of crystallization, which escapes rapidly at laboratory temperature and atmospheric pressure. During this drying the crystals lose their transparency and take on the opaque appearance exhibited by bodies which have effloresced.

[1] *Loc. cit.*

Dipotassium Acetamide, CH_3CONK_2, is probably formed when solutions containing 2 molecules of potassium amide and 1 molecule of acetamide are brought together. The product, however, is so extremely soluble that it cannot be drained of mother-liquor for analysis. At the temperature of the ammonia-bath it crystallizes from very concentrated solutions to a nearly solid mass, which melts as soon as the temperature is allowed to rise.

Monopotassium Phenylacetamide, $C_6H_5CH_2CONHK.nNH_3$.— When phenylacetamide and potassium amide are brought together in molecular proportions and the solution is cooled to $-33°$, a crop of beautiful, needle-like crystals fills the tube. At higher temperatures these crystals dissolve very easily. Upon drying they lose their luster, and must consequently contain ammonia of crystallization.

0.1067 gram salt gave 0.0540 gram K_2SO_4.
0.1491 gram salt gave 0.0755 gram N.

	Calculated for $C_6H_5CH_2CONHK$.	Found.
K	22.60	22.72
N	8.11	5.06

Monopotassium Benzamide, C_6H_5CONHK.—When equimolecular quantities of benzamide and potassium amide are brought together in ammonia solution a bulky, crystalline precipitate of the monopotassium salt is formed. The compound which apparently does not contain ammonia of crystallization, is somewhat soluble in ammonia and in excess of the acid amide. It is also soluble in excess of the basic amide.

I. 0.0765 gram salt gave 0.0418 gram K_2SO_4.
   0.1592 gram salt gave 0.01384 gram N.
II. 0.0576 gram salt gave 0.0309 gram K_2SO_4.
   0.0865 gram salt gave 0.00482 gram N.

	Calculated for C_6H_5CONHK.	I.	II.
		Found.	
K	24.60	24.54	24.10
N	8.81	8.70	5.58

Dipotassium Benzamide, $C_6H_5CONK_2$, is formed as a bulky, crystalline precipitate when two molecular weights of potassium amide are mixed with one molecular weight of benz-

amide in ammonia solution. The salt is somewhat soluble.

	Calculated for $C_6H_5CONK_2$.	Found.
K	39.66	....
N	7.11	7.12

Monopotassium Benzenesulphonamide, $C_6H_5SO_2NHK$.—Upon adding an equivalent quantity of the acid amide to potassium amide a solid substance forms at the junction of the two solutions and completely separates them. Upon agitation, however, everything passes into solution, and after a short time colorless, well-formed crystals separate, especially from the cold solution. The salt is fairly soluble in ammonia, very easily soluble in excess of acid amide, but insoluble in excess of the basic amide. The crystals lost neither form nor luster when heated to the temperature of boiling water. They must consequently be free from ammonia of crystallization.

    I. 0.3623 gram salt gave 0.1598 gram K_2SO_4.
    II. 0.1942 gram salt gave 0.0824 gram K_2SO_4.
    III. 0.0850 gram salt gave 0.0380 gram K_2SO_4.
        0.1939 gram salt gave 0.0131 gram N.

	Calculated for $C_6H_5SO_2NHK$.	I.	Found. II.	III.
K	20.04	19.79	19.05	20.10
N	7.19	....	....	6.78

Dipotassium Benzenesulphonamide, $C_6H_5SO_2NK_2$.—Benzenesulphonamide, when added to an excess of potassium amide, produces a very bulky, amorphous precipitate which refuses to settle and which consequently cannot be well washed. In the case of the preparation numbered II below, the liquid was evaporated completely from the precipitate in the hope of getting the substance into a better condition for washing. The result was that a sticky, amorphous mass remained clinging to the walls of the tube in such a condition as to render thorough washing impracticable. The low results obtained may very well be due to the presence of the monopotassium salt, which was protected during the process of washing by the insoluble dipotassium salt.

    I. 0.2599 gram salt gave 0.1852 gram K_2SO_4.
    II. 0.1702 gram salt gave 0.1132 gram K_2SO_4.

	Calculated for $C_6H_6SO_2NK_2$.	Found. I.	II.
K	33.53	32.00	29.80

Monopotassium Paratoluenesulphonamide,
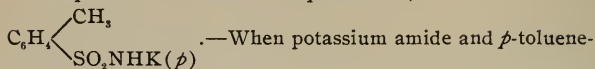
$C_6H_4{\Large\langle}{}^{CH_3}_{SO_2NHK(p)}$.—When potassium amide and *p*-toluene-

sulphonamide are mixed an amorphous precipitate is formed which is insoluble in excess of either acid or basic amide. The salt for which the analysis is given below was made by adding potassium amide solution to a solution of the acid amide until a sufficient quantity of the monopotassium compound for analysis was obtained.

0.1058 gram salt gave 0.0392 gram K_2SO_4.

0.1505 gram salt gave 0.0172 gram N.

	Calculated for $C_7H_7SO_2NHK$.	Found.
K	16.31	16.64
N	6.71	11.42

Monopotassium Metamethoxybenzenesulphonamide,

$C_6H_4{\Large\langle}{}^{O—CH_3}_{SO_2NHK(m)}$.—A crop of small, well-formed crystals
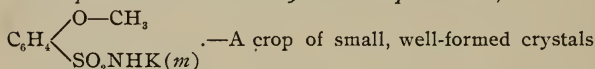
without ammonia of crystallization is formed when equimolecular quantities of potassium amide and metamethoxybenzenesulphonamide are brought together in ammonia solution. The salt is distinctly soluble.

0.1149 gram salt gave 0.0436 gram K_2SO_4.

0.1782 gram salt gave 0.1849 gram $BaSO_4$.

	Calculated for $C_7H_7OSO_2NHK$.	Found.
K	17.36	17.03
S	14.21	14.24

Dipotassium Metamethoxybenzenesulphonamide,

$C_6H_4{\Large\langle}{}^{OCH_3}_{SO_2NK_2(m)}$.—An insoluble, apparently amorphous
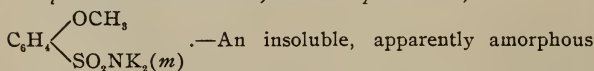
precipitate of the dipotassium salt of metamethoxybenzenesulphonamide is formed when 1 molecule of the acid amide is added to 2 molecules of potassium amide. The precipitate

settles well and is easily washed for analysis. The salt contains no ammonia of crystallization.

0.1256 gram salt gave 0.0822 gram K_2SO_4.
0.0595 gram salt gave 0.0518 gram $BaSO_4$.

	Calculated for $C_7H_7OSO_2NK_2$.	Found.
K	29.73	29.39
S	12.13	11.96

Monopotassium Paramethoxybenzenesulphonamide,

$C_6H_4 \begin{cases} OCH_3 \\ SO_2NHK(p) \end{cases}$.—When potassium amide is added to a

solution of paramethoxybenzenesulphonamide a precipitate is formed which is soluble in excess of the acid amide. The salt does not settle well, is crystalline and somewhat soluble in ammonia. It does not contain ammonia of crystallization.

   I. 0.0517 gram salt gave 0.0042 gram N.
  II. 0.1740 gram salt gave 0.00936 gram N.
 III. 0.0665 gram salt gave 0.0053 gram N.
     0.0747 gram salt gave 0.0258 gram K_2SO_4.

	Calculated for $C_7H_7OSO_2NHK$.	I.	Found. II.	III.
K	17.36	....	....	16.35
N	6.23	8.11	5.38	7.98

Dipotassium Paramethoxybenzenesulphonamide,

$C_6H_4OCH_3SO_2NK_2$, is presumably formed as a very bulky, insoluble precipitate when 1 molecule of paramethoxybenzenesulphonamide is added to 2 molecules of potassium amide. The precipitate fills the whole tube and refuses to settle. It was therefore impracticable to wash the precipitate for analysis.

Sulphamide, $SO_2 \begin{cases} NH_2 \\ NH_2 \end{cases}$.—Sulphamide[1] was prepared ac-

cording to the directions given by Traube.[2] It is very soluble in liquid ammonia, even deliquescing in the vapor given off by the cold liquid. Indeed, it absorbs ammonia so rapidly that the liquid in the second arm of the closed preparation-tube

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[1] A sample of sulphamide made by Schuchardt was found to contain over 90 per cent of ammonium sulphate.

[2] Ber. d. chem. Ges., **26**, 607 (1893).

boiled vigorously even when covered with ice. The resulting solution is viscid and colorless, but when diluted forms a clear, mobile liquid. The solution discharges the red color produced in an ammonia solution of phenolphthalein by potassium amide, and is a good conductor of electricity.

Since the molecule of sulphamide contains four amide hydrogen atoms it would seem that it perhaps ought to be possible to prepare four potassium sulphamide derivatives. Investigation, however, has proved the existence of the mono- and dipotassium salts only.

Monopotassium Sulphamide, $SO_2N_2H_3K$.—When potassium amide is added to a solution of an equivalent quantity of sulphamide an amorphous, white precipitate is formed, which is not appreciably soluble in excess of either acid or basic amide. A determination of potassium in which losses were known to occur during the analysis, resulted as follows :

0.0762 gram salt gave 0.0451 gram K_2SO_4.

	Calculated for $SO_2N_2H_3K$.	Found.
K	29.10	26.70

Further analyses of this salt have not yet been made for the reason that the small quantity of the acid amide prepared was too soon exhausted.

Dipotassium Sulphamide, $SO_2N_2H_2K_2$.—A bulky, amorphous precipitate of the dipotassium salt of sulphamide is formed when 1 molecule of the acid amide is added to 2 molecules of potassium amide. Because of the difficulty encountered in washing the bulky precipitate, the purity of the sample submitted to analysis was not assured. The solvent was completely evaporated from the precipitate in an attempt to get it into better condition for washing. This was not successful, however, for the precipitate then remained plastered to the walls of the tube in such a form as to prevent efficient action of the washing liquid.

0.2069 gram salt gave 0.02816 gram N and 0.2928 gram $BaSO_4$.

	Calculated for $SO_2N_2H_2K_2$.	Found.
N	16.29	13.78
S	18.59	19.43

Losses of nitrogen were known to have occurred during the progress of the analysis.

In another experiment, in which the quantity of potassium amide used was in considerable excess of the amount necessary for the formation of the dipotassium salt, a determination of the potassium in the product resulted as follows :

0.1385 gram salt gave 0.1364 gram K_2SO_4.

	Calculated for $SO_2N_2H_2K_2$.	Found.
K	45.41	44.26

An attempt was made to obtain a salt in which more than 2 atoms of potassium are present in the molecule. To this end 1 molecule of sulphamide was added gradually to somewhat more than 4 molecules of potassium amide, and the mixture with the excess of basic amide was, after being thoroughly shaken, allowed to stand for five days at laboratory temperature. A bulky, amorphous, insoluble precipitate, similar in appearance to those obtained above, was the result. The product could not be thoroughly washed.

0.0570 gram salt gave 0.0630 gram K_2SO_4.

	Calculated for $SO_2N_2H_2K_2$.	Found.
K	45.41	49.62

Hence, it seems that compounds containing more than 2 atoms of the metal cannot be formed under these circumstances. The high results obtained for the potassium content of the preparation may be due to the incomplete removal of the admixed potassium amide, or, it may be, that some tri- or even tetrapotassium salt is formed in the presence of a large excess of the basic amide which is then not entirely decomposed, hydrolyzed, and removed during the subsequent washing.

Urea, CON_2H_4.—The considerations concerning the possible existence of four potassium derivatives of sulphamide apply to the case of urea, which, likewise, contains four amide hydrogen atoms. As in the previous case, however, investigation has shown that the tri- and tetrametallic derivatives are not formed.

Monopotassium Urea, CON_2H_3K.—Upon mixing solutions containing equivalent quantities of urea and potassium amide a white precipitate immediately forms which fills the whole arm of the preparation-tube as an amorphous mass. If, however, the potassium amide be added to the urea, a drop at a time, then a tough osmotic membrane of the potassium salt forms around each drop, enclosing it and protecting it from further action of the acid amide. These globules are easily broken up by agitation, however, and the precipitate goes into solution in the excess of urea. At a certain stage in the process of adding the basic amide the conditions become such that a cloudiness is produced. Cooling the solution at this stage causes the disappearance of the cloudiness, which appears again on warming the tube. At somewhat greater concentration, and at the temperature of the laboratory, two liquid layers appear. If the tube is again cooled the contents of the tube again become homogeneous. On warming the tube the cloudiness again appears, followed by the formation of the two liquid layers. In more concentrated solutions the separation into two liquid layers cannot be accomplished. After the addition of the full equivalent of potassium amide, the monopotassium salt slowly separates out on the walls and bottom of the tube in the form of minute, colorless crystals. Unless the addition of the potassium amide is carefully carried out the precipitate is formed as an amorphous mass which cannot be well washed, a fact which probably accounts for the divergent analytical results.

    I. 0.2494 gram salt gave 0.2580 gram K_2SO_4.
    II. 0.3645 gram salt gave 0.3435 gram K_2SO_4.
    III. 0.2374 gram salt gave 0.2104 gram K_2SO_4.
    IV. 0.3286 gram salt gave 0.0980 gram N.
    V. 0.1856 gram salt gave 0.0544 gram N.
       0.1210 gram salt gave 0.1017 gram K_2SO_4.
    VI. 0.1316 gram salt gave 0.0364 gram N.
    VII. 0.1149 gram salt gave 0.1000 gram K_2SO_4.
    VIII. 0.2874 gram salt gave 0.0864 gram N.

Calculated for CON_2H_3K.	I.	II.	III.	Found. IV.	V.	VI.	VII.	VIII.
K	39.75	46.45	42.30	39.80	....	37.75	....	39.74	....
N	28.50	....	....	....	29.80	29.30	27.67	....	30.45[1]

[1] The specimen used for making this determination was not free from ammonia.

Dipotassium Urea, $CON_2H_2K_2$.—If the order of the process described above for bringing the solutions together be reversed, that is, if the acid amide be poured into the basic amide solution, a permanent, gelatinous precipitate is produced, which the analyses show to be probably a mixture of the dipotassium salt with more or less of the monopotassium compound. An ammonia solution of urea is a very poor conductor of electricity. Urea must therefore be regarded as a very weak acid from which it follows that hydrolysis of the dipotassium salt may account for the divergent analytical results here recorded.

Analyses of products formed by the interaction of 1 molecule of urea with 2 molecules of potassium amide are as follows :

    I. 0.1301 gram salt gave 0.1685 gram K_2SO_4.

    II. 0.1058 gram salt gave 0.0244 gram N.

    III. 0.1205 gram salt gave 0.0275 gram N.

    IV. 0.1341 gram salt gave 0.0307 gram N.

    V. 0.1205 gram salt gave 0.0266 gram N.

    VI. 0.1288 gram salt gave 0.1370 gram K_2SO_4.

    VII. 0.0713 gram salt gave 0.0770 gram K_2SO_4.

    VIII. 0.2041 gram salt gave 0.0500 gram N.

    IX. 0.1761 gram salt gave 0.0374 gram N.

    X. 0.2522 gram salt gave 0.0545 gram N.

    XI. 0.1796 gram salt gave 0.0365 gram N.

	Calculated for $CON_2H_2K_2$.	I.	II.	III.	Found. IV.	V.	VI.
K	57.42	58.11	....	....	....	....	47.60
N	20.60	....	23.10	22.80	22.94	22.05	....

	Calculated for $CON_2H_2K_2$.	VII.	VIII.	Found. IX.	X.	XI.
K	57.42	48.40	....	....	....	....
N	20.60	....	24.53	21.28	21.59	20.30

In two experiments in which 1 molecule of urea was added to something over 3 molecules of potassium amide, and the tubes were allowed to stand several days to complete the reaction, analysis of the gelatinous precipitate gave the following results :

    I. 0.1200 gram salt gave 0.0248 gram N.

    II. 0.0779 gram salt gave 0.995 gram K_2SO_4.

	Calculated for $CON_2H_2K_2$.	Found.	
		I.	II.
K	57.42	....	57.33
N	20.60	20.65	....

Potassium Saccharin.—When potassium amide is added to a solution of saccharin a gelatinous precipitate is formed which surrounds each drop of the basic amide solution as an osmotic membrane. On agitation the precipitate dissolves in excess of the acid imide. Further addition of the basic amide produced a permanent precipitate, which gave widely divergent analytical results. In five experiments the precipitate formed by the addition of 1 molecule of potassium amide to 1 molecule of saccharin gave from 22.20 to 26.67 per cent potassium. The calculated percentage of potassium in $C_6H_4SO_2CONK$ is 17.67. When 2 molecules of potassium amide were added to 1 of saccharin, two experiments gave respectively 33.08 and 30.20 per cent potassium, while three further experiments gave 11.69, 9.80, and 11.74 per cent sulphur. It seems probable that the compound $C_6H_4\begin{smallmatrix}CONHK\\SO_2NHK\end{smallmatrix}$ is formed, but the exhaustion of the supply of saccharin prevented further investigation along this line.

Other Potassium Derivatives.

Attempts were made to prepare potassium salts of a considerable number of other acid amides, but while action evidently took place in each instance, for various reasons no products were isolated.

Formamide.—When a solution of 1 molecule of potassium amide is added to 1 molecule of formamide, and the solution is cooled in a bath of liquid ammonia, a crop of beautiful needle-like crystals separate from the solution. Decomposition accompanied by the evolution of hydrogen immediately sets in, however, and in a short time the crystals disappear and cannot be again obtained.

Dichloracetamide.—On mixing dichloracetamide and potassium amide the solution rapidly became strongly colored. After a time a brick-red precipitate separated, but this soon

disappeared and the contents of the tube became less and less promising as time passed.

Thioacetamide.—When potassium amide solution is added to a solution of thioacetamide a precipitate is formed which quickly dissolves in excess of the acid amide. The mono-potassium salt, if such is formed, is so very soluble in ammonia that a product for analysis could not be isolated. With potassium amide in excess a permanent precipitate is produced, but the attempt to purify this substance for analysis was not made.

Cyanacetamide.—On adding 1 molecule of potassium amide to 1 molecule of cyanacetamide a precipitate is produced which immediately dissolves when the contents of the tube are mixed. Cooling caused no separation of crystals. On evaporating the solution a thick, viscous residue was left, which dried finally to a frothy mass which foamed up and almost filled the tube. This residue is very deliquescent in ammonia vapor. At a certain stage during the deliquescence, crystalline nuclei made their appearance and gradually spread through the mass only to disappear again as the absorption of ammonia continued. This very soluble, deliquescent substance is in all probability the monopotassium salt of cyanacetamide. Attempts were not made to prepare the dipotassium salt.

Parachlorbenzamide.—When potassium amide is added to a solution of parachlorbenzamide, a fugitive, colored precipitate is formed which dissolves instantly in excess of the acid amide to form a red solution. When the acid amide is added to the potassium amide a green solution results, with no indication of a precipitate. From the red solution formed by mixing equimolecular quantities of the acid and basic amides it is possible, in the cold and from very concentrated solutions, to obtain an exceedingly soluble mass of crystals, presumably of monopotassium parachlorbenzamide. The attempt to separate them for analysis was not made.

Succinimide gave a precipitate with potassium amide, but on standing the precipitate became so strongly colored and unpromising in appearance that the experiment was discontinued.

Thiourea.— The behavior of thiourea solutions, when brought into contact with potassium amide, is almost identical with that exhibited by ordinary urea. The precipitates are much more gelatinous, however, and much less stable than the urea compounds, suffering decomposition at the temperature used for drying the latter. Indeed, so much difficulty was encountered in this respect that no concordant analytical results have been obtained.

Allylthiourea.—The addition of 1 molecule of potassium amide to 1 molecule of the acid amide produced no permanent precipitate. When the solution is very concentrated and is kept cooled for some time the viscous residue changes into a mass of crystals, which very soon liquefy on being removed from the bath of liquid ammonia. With potassium amide in excess a much less soluble product is obtained.

Trinitraniline (*Picramide*).—The well-known acid properties of trinitrophenol and the fact that trinitraniline is a fair conductor[1] of electricity when in solution in liquid ammonia, suggests the possibility of metathetic action between the latter and potassium amide. Picramide is very easily soluble in ammonia, with which it forms a deep-red solution. On adding potassium amide to a solution of picramide an amorphous, dark-colored precipitate is formed, which quickly dissolves in excess of the acid amide. With further additions of the basic amide, a good crop of well-formed crystals are deposited. The crystals slowly disappear, however, even when the tube is kept cold. After an hour or two they have completely disappeared and cannot again be obtained. Evaporation of the solvent leaves a strongly colored, viscous mass, from which a product for analysis could not be obtained. It seems probable that metathetic action actually takes place but that the result is obscured by deep-seated changes which rapidly follow.

Metanitroparatoluidine, with potassium amide, gave a strongly colored solution from which no product for analysis could be separated.

[1] Measurements by Franklin and Kraus.

Sodium Salts.

Metallic sodium dissolves readily in liquid ammonia, forming a blue solution to all outward appearances, identical with the potassium solution described above.

Sodium amide formed by the decomposition of sodammonium is a perfectly colorless substance which separates from the ammonia solution as well-formed, granular crystals. An analysis of a specimen thus prepared gave the following results :

0.0702 gram amide gave 0.1264 gram Na_2SO_4.

0.0366 gram amide gave 0.01286 gram N.

	Calculated for $NaNH_2$.	Found.
Na	58.95	58.38
N	35.90	35.13

Monosodium Acetamide, $CH_3CONHNa.nNH_3$.—This compound is formed when equimolecular quantities of sodium amide and acetamide are brought together in ammonia solution. It dissolves readily in ammonia, but is not so soluble as the potassium salt. Like the potassium derivative, it separates with ammonia of crystallization. Since, in the preparation of the specimen for which the analysis is given, considerable excess of acetamide was used which could not be removed by washing on account of the ready solubility of the salt, contamination with acetamide probably accounts for the results obtained.

	Calculated for $CH_3CONHNa$.	Found.
Na	28.43	21.83

Sodium acetamide is also formed by the action of a solution of acetamide on metallic sodium. The action is vigorous and is accompanied by the evolution of hydrogen. The salt separates as a crop of well-formed crystals from the concentrated solution.

Magnesium Salts.

If the condition of acid amides in solution in liquid ammonia is analogous to the condition of the oxygen acids in aqueous solution, then solutions of the former should attack at least the more electropositive metals with the evolution of

hydrogen. That such action does take place very readily in the case of sodium and magnesium, and to some slight extent in the case of zinc, has already been pointed out by Franklin and Kraus.[1]

While acetamide acts readily on sodium, potassium and magnesium, experiments in which zinc, iron, aluminum, and copper were left in contact with acetamide solution for six months, show these metals to be entirely unaffected. Benzenesulphonamide acts rapidly on sodium and potassium, more slowly upon magnesium, and very slowly on zinc. The zinc is soon coated with a yellowish, insoluble crust, presumably of zinc benzenesulphonamide, which stops further action.

Of the acid amides whose action on magnesium has been tested, acetamide, benzenesulphonamide, benzoic sulphinide, benzamide, phenylacetamide, cyanacetamide, and cyanamide have been found to attack the metal while formamide, toluenesulphonamide, succinamide, and sulphamide have been found to be without appreciable action. Magnesium, as well as sodium and potassium, are also readily attacked by solutions of ammonium salts. In solutions of ammonium nitrate, magnesium dissolves rapidly, and after a time well-formed crystals of magnesium nitrate separate from the solution. Ammonium bromide attacks the metal with the simultaneous separation of the nearly insoluble magnesium bromide.

Magnesium Acetamide, $(CH_3CONH)_2Mg.4NH_3$. — When magnesium is added to a solution of acetamide the metal dissolves with the evolution of an equivalent amount of hydrogen. A clear, colorless solution is formed from which, after several hours, well-formed, colorless, granular crystals of magnesium acetamide containing 4 molecules of ammonia of crystallization separate. The salt is somewhat soluble in ammonia. It effloresces readily at laboratory temperature when the tube is opened and the ammonia is allowed to escape. When exposed to the air the dry salt absorbs water rapidly and forms a sticky mass, which does not dissolve completely in water but dissolves readily in hydrochloric acid.

    I. 0.4577 gram crystallized salt lost 0.1443 gram NH_3.

       0.3134 gram dry salt gave 0.2460 gram $Mg_2P_2O_7$.

[1] This JOURNAL, **23**, 304 (1900).

II. 0.5930 gram crystallized salt lost 0.1950 gram NH_3.
0.3980 gram dry salt gave 0.2960 gram $Mg_2P_2O_7$.

III. 0.2254 gram crystallized salt lost 0.0878 gram NH_3.
0.1376 gram dry salt gave 0.1092 gram $Mg_2P_2O_7$ and
0.0270 gram N.

IV. 0.2090 gram crystallized salt lost 0.0620 gram NH_3.
0.1406 gram dry salt gave 0.1045 gram $Mg_2P_2O_7$ and
0.0273 gram N.

	Calculated for $(CH_3CONH)_2Mg.4NH_3$	I.	II.	III.	IV.
			Found.		
NH_3	32.69	31.53	32.88	38.95[1]	29.67[2]

	Calculated for $(CH_3CONH)_2Mg.$	I.	II.	III.	IV.
			Found.		
Mg	17.14	17.02	16.08	17.36	16.08
N	20.00	....	....	19.61	19.44

I. 0.0538 gram magnesum liberated 62.4 cc. hydrogen measured over water at 24° and 741 mm. barometric pressure.

II. 0.0692 gram magnesium liberated 77.4 cc. hydrogen measured over water at 27° and 740 mm. barometric pressure.

	Found for 1 equivalent of magnesium.	
	I.	II.
H	1.08	1.04

Magnesium Benzenesulphonamide, $(C_6H_5SO_2NH)_2Mg.nNH_3$. —This compound is produced in the form of colorless crystals containing ammonia of crystallization when metallic magnesium is dissolved in an ammonia solution of benzenesulphonamide. The salt is slightly soluble. The effloresced salt gave the following analytical results.

0.1966 gram salt gave 0.0640 gram $Mg_2P_2O_7$ and 0.0159 gram N.

	Calculated for $(C_6H_5SO_2NH)_2Mg.$	Found.
Mg	7.28	7.05
N	8.39	8.11

Magnesium Cyanamide, $CNNMg.nNH_3$.—Cyanamide in solution in liquid ammonia immediately attacks metallic magnesium with the evolution of hydrogen gas. After a time the salt, which is moderately soluble, separates in the form of well-formed, granular crystals. The salt was recrystallized

[1] This specimen was known to contain an excess of ammonia.
[2] The salt was dried in a bath of ice and salt. The crystals showed distinct efflorescence.

into the second arm of the apparatus, washed, and dried for analysis. The crystals contain ammonia of crystallization, as was shown by their efflorescence when the ammonia was allowed to escape. The crystals assumed a reddish tint on standing.

0.0673 gram salt gave 0.02935 gram N.

	Calculated for CNNMg.	Found.
N	43.75	43.61

Summary of Results.

It has been shown in this investigation that the relation borne by the acid amides and the metallic amides toward liquid ammonia as a solvent is strikingly analogous to the well-known relations borne by the ordinary acids and bases to water.

Metathetic reactions between many acid amides and potassium amide in solution in liquid ammonia take place with all the facility which marks the interaction of ordinary acids and bases in aqueous solution.

Acid amides in solution in liquid ammonia attack potassium and sodium, and in some cases magnesium, with the evolution of hydrogen and the formation of the metallic derivatives of the acid amides.

The following salts have been prepared :

Monopotassium acetamide,
Monopotassium phenylacetamide,
Monopotassium benzamide,
Dipotassium benzamide,
Monopotassium benzenesulphonamide,
Dipotassium benzenesulphonamide,
Monopotassium toluenesulphonamide,
Monopotassium metamethoxybenzenesulphonamide,
Dipotassium metamethoxybenzenesulphonamide,
Monopotassium paramethoxybenzenesulphonamide,
Monopotassium sulphamide,
Dipotassium sulphamide,
Monopotassium urea,
Dipotassium urea,
Monosodium acetamide,
Magnesium acetamide,
Magnesium benzenesulphonamide,
Magnesium cyanamide.

In conclusion, the authors wish to express their appreciation of the kindness of Professor Arthur Lachman in placing the laboratories of the University of Oregon at their disposal for the prosecution of a portion of this work.

ON THE ACTION OF ETHYLENE DIBROMIDE ON PARANITROSODIMETHYLANILINE.

BY HENRY A. TORREY.

By heating ethylene dibromide with dimethylaniline at 100° C. for some time, Schoop[1] found that one of the hydrogen atoms in the ring was attacked and a dibenzyl derivative was obtained.

When the para position is occupied as in paranitrosodimethylaniline, the hydrogen of the ring is not attacked, a dibenzyl derivative is not obtained, but the nitroso group itself is acted upon, as is shown in the following study of the action of ethylene dibromide.

In a study of the action of benzoyl chloride on p-nitrosodimethylaniline, Ehrlich and Cohn[2] found that an addition-product is formed for which they give two possible formulas :
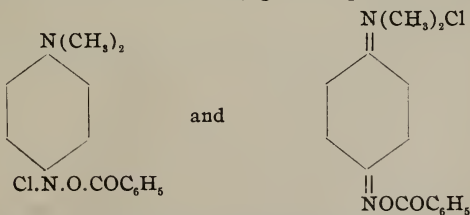
And Knorr,[3] by allowing a benzene solution of p-nitrosodimethylaniline and methyl iodide to stand for some time, obtained a similar addition-product, to which, on account of the nature of decomposition-products obtained by the action of sodium hydroxide, he assigns the formula :

[1] Ber. d. chem. Ges., **13**, 2196.
[2] *Ibid.*, **26**, 1756.
[3] *Ibid.*, **30**, 933.

$$N(CH_3)_2I$$

$$N.OCH_3$$

When ethylene dibromide acts upon nitrosodimethylaniline no such addition-product is obtained, although such a body may very likely be formed as an intermediate product. When *p*-nitrosodimethylaniline is warmed on the water-bath for a short time with a large excess of ethylene dibromide at least two products are obtained, the hydrobromide of *p*-nitrosodimethylaniline and a body consisting of 2 molecules of the base united by an ethylene residue. The reaction may be represented as follows:

$$4NO.C_6H_4N(CH_3)_2 + BrCH_2.CH_2Br =$$
$$2NO.C_6H_4N(CH_3)_2.HBr + [ON.C_6H_4.N(CH_3)_2]_2C_2H_2.$$
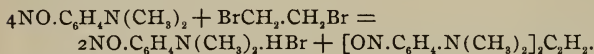
The identity of the *p*-nitrosodimethylaniline hydrobromide was proved by analysis and conversion into the free base by sodium carbonate.

The second and more interesting product of the reaction, and which one may name dinitrosodimethylanilineethylene is a beautiful deep-red, crystalline compound, melting, with decomposition, at about 234° C.

That this product is not a dibenzyl derivative is shown by its great instability toward mineral acids, for although it is easily soluble in these acids it is impossible to recover the base by neutralization. Further, in his study of the formation of tetramethyldiamidodibenzyl by the action of ethylene dibromide on dimethylaniline, Schoop found that it was necessary to heat the mixture for eight days, while the action of ethylene dibromide on the less basic *p*-nitrosodimethylaniline is complete in as many minutes.

The most probable interpretation of the reaction is that the nitroso group is concerned in the reaction and that an addi-

tion-product is first formed, similar to those formed in the action of benzoyl chloride or methyl iodide, from which hydrobromic acid is split off, which is then taken up by the *p*-nitrosodimethylaniline which is still unacted upon. The ethylene dibromide might attach itself in three different ways, as follows:

$$N—OCH_2.CH_2O—N$$

$$N(CH_3)_2Br \qquad N(CH_3)_2Br$$

I.

$$Br—NOCH_2CH_2.ONBr$$

$$N(CH_3)_2 \qquad N(CH_3)_2$$

$$Br \qquad\qquad Br$$
$$—NOCH_2CH_2ON—$$

$$—N(CH_3)_2 (CH_3)_2N—$$
Quinone formula.

II.

$$O \quad Br \qquad Br \quad O$$
$$N—CH_2.CH_2—N$$

and

$$N(CH_3)_2 \qquad N(CH_3)_2$$

III.
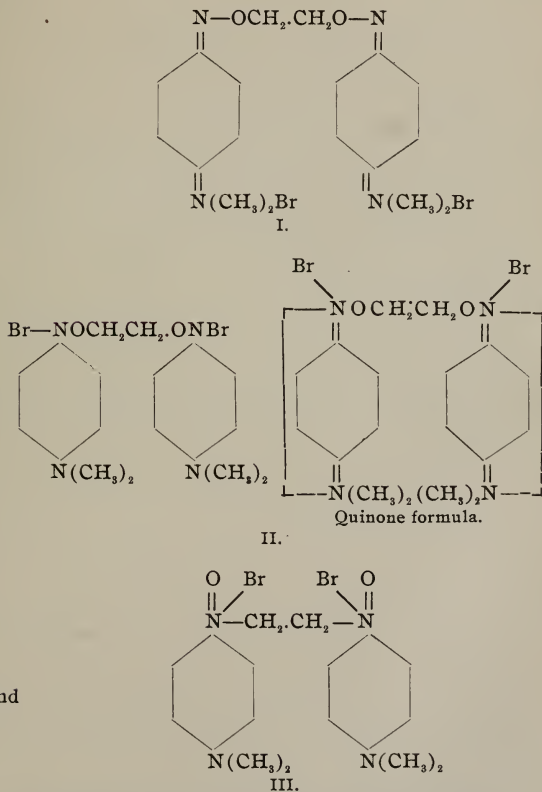
III. may also, of course, be given the quinoid form.

From a body having formula I. or II., by elimination of hydrobromic acid, a compound with the following formula would probably be obtained :

or
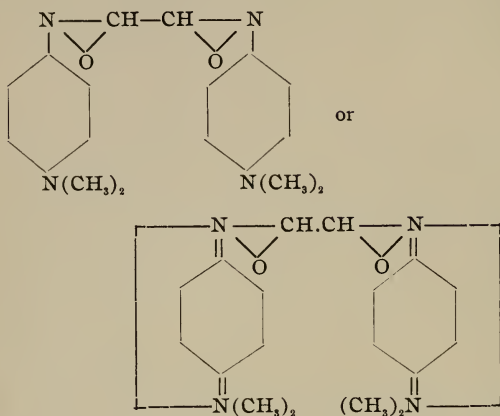
and III would give a body in which the nitrogen of the nitroso group is quinquivalent but that of the amino group trivalent, thus :
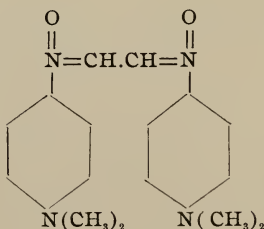
or in which, according to the quinone formula, both nitrogen atoms are quinquivalent.

That the union is not through the amino groups, thus,

$$\begin{matrix} O & & O \\ \| & & \| \\ N & & N \end{matrix}$$

(CH₃)₂N=CH.CH=N(CH₃)₂
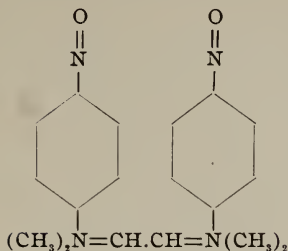
is shown by the fact that the body, though easily broken down by mineral acids, still does form salts with some organic acids from which the original base can again be recovered by alkalies. With picric acid, for instance, a salt is obtained containing two equivalents of the acid, and which, by treatment with sodium hydroxide, gives the free body again.

The instability of this ethylene derivative toward small quantities of mineral acids is shown by the course of the reaction when it is carried on in alcoholic solution (85 per cent). Under these conditions the red dinitrosodimethylaniline-ethylene, which is first formed, is broken down, probably by the hydrobromic acid from partial hydrolysis of the hydrobromide of *p*-nitrosodimethylaniline, the nitroso groups are reduced at the expense of the hydrolyzed ethylene residue and tetramethyldiamidoazoxybenzene is formed, as is shown in the experimental part of this paper. That it is the salt of the nitrosodimethylaniline which brings about this decomposition in alcoholic solution is shown by the fact that when the red dinitrosodimethylanilineethylene is heated with *p*-nitrosodimethylaniline hydrochloride and alcohol the same reduction takes place, and tetramethyldiamidoazoxybenzene is formed, and that when it is heated with alcohol alone it is unchanged.

In studying the action of dilute mineral acids on the di-paranitrosodimethylanilineethylene, it was found that dilute nitric acid was best adapted to this purpose, for by the use of this acid the separation of the different products of the reaction was facilitated, since the salt of paranitrosodimethylaniline, which is formed in this reaction, is, in the case of nitric acid, insoluble in water, while the other products remain in solu-

tion. The formation of *p*-nitrosodimethylaniline nitrate shows that the action of this reagent is partly hydrolytic, while the other products formed indicate that an oxidation of the ethylene residue and a reduction of the other nitrosodimethylaniline group have taken place. By neutralizing the filtrate from the nitrate a yellow body was obtained which melted at 255° to 256°, and contained no oxygen. The exact nature of this substance has not as yet been determined. The study of this body is being continued in collaboration with others in this laboratory. The filtrate from the yellow body responds to the tests for formic acid. The action of dilute nitric acid on diparanitrosodimethylanilineethylene is, therefore, a rather complex one. First of all, a partial hydrolysis takes place, the nitrate of *p*-nitrosodimethylaniline is formed and separates from solution, the other nitroso group is reduced at the expense of the hydrolyzed ethylene residue which is itself oxidized by the oxygen of the nitroso group and the nitric acid to formic acid.

EXPERIMENTAL PART.

Action of Ethylene Dibromide on Paranitrosodimethylaniline.

This reaction goes most smoothly when a large excess of ethylene dibromide is used. Forty grams of *p*-nitrosodimethylaniline were heated with 160 grams of ethylene dibromide for about six minutes on the steam-bath until the mixture had lost its green color and the reddish-brown reaction-product had separated copiously. It was then immediately cooled down and alcohol was added to stop the reaction, which is likely to become violent unless some such precaution is taken ; or better, the mixture is kept at a temperature of 80° to 90° C., by alternate heating and cooling, and the reaction is allowed to go for a longer period (fifteen to twenty minutes). The mixture was then collected upon a filter, washed with alcohol, then with alcohol containing sodium hydroxide, and finally boiled out with alcohol and washed with ether. For further purification it was recrystallized from hot amyl alcohol, and washed with ethyl alcohol. By this treatment a beautiful garnet-red body, which crystallized in

needles, was obtained. After drying in air, and finally in a desiccator, it was analyzed with the following results:

I. 0.1212 gram substance gave, on combustion, 0.2975 gram CO_2 and 0.0816 gram H_2O.

II. 0.1202 gram substance gave 0.2927 gram CO_2 and 0.0817 gram H_2O.

III. 0.1110 gram substance gave 0.2728 gram CO_2 and 0.0730 gram H_2O.

IV. 0.0992 gram substance gave 0.2419 gram CO_2 and 0.0640 gram H_2O.

V. 0.1512 gram substance gave 0.3662 gram CO_2 and 0.0934 gram H_2O.

VI. 0.1800 gram substance gave 27.0 cc. moist nitrogen at 20° C. and 761 mm. pressure.

VII. 0.1881 gram substance gave 29.6 cc. moist nitrogen at 25° C. and 753 mm. pressure.

	Calculated for $(NO.C_6H_4N(CH_3)_2)_2C_2H_2$.	I.	II.	III.	Found. IV.	V.	VI.	VII.
C	66.26	66.94	66.41	67.02	66.50	66.05	....	....
H	6.74	7.48	7.55	7.30	7.16	6.86	....	....
N	17.18	....	....	....	....	....	17.18	17.38

The body was found to contain no bromine. The analytical results show that the substance has the composition $C_{18}H_{22}N_4O_2$. As has been suggested earlier in this paper, it is most probable that the body is the result of the union of 2 molecules of *p*-nitrosodimethylaniline by means of an intermediate hydrocarbon group thus:

$$ON.C_6H_4N(CH_3)_2—C_2H_2—N(CH_3)_2C_6H_4.NO.$$
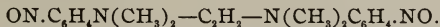
This substance may properly be called di-*p*-nitrosodimethylanilineethylene. The hydrobromic acid formed during the reaction is taken up by the free nitrosodimethylaniline present with the formation of the hydrobromide of this base. This body was separated from the reaction-mixture and identified as described below. The reaction of ethylene dibromide on *p*-nitrosodimethylaniline consists, thus, in the splitting off of 2 molecules of hydrobromic acid, the union of 2 molecules of the base with the ethylene residue and the subsequent formation of the hydrobromide of *p*-nitrosodimethylaniline, and may be expressed as follows:

$$4NO.C_6H_4N(CH_3)_2 + C_2H_4Br =$$
$$[NO.C_6H_4.N(CH_3)_2]_2C_2H_2 + 2NO.C_6H_4N(CH_3)_2HBr.$$
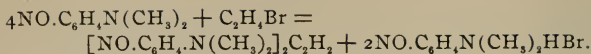
Properties of Di-p-nitrosodimethylanilineethylene.—The body crystallizes in deep-red needles from amyl alcohol, which decompose at 230° to 240° C., the temperature depending on the rapidity of the heating. It is soluble in chloroform and glacial acetic acid, very slightly soluble in ethyl alcohol and insoluble in water. It is very easily soluble in dilute mineral acids, by all of which, however, it seems to be decomposed. From its chloroform solution a well characterized picric acid salt was obtained. No precipitate was obtained when its aqueous hydrochloric acid solution was neutralized by sodium hydroxide or carbonate. It is reduced by zinc and acetic acid, and by sodium amylate in amyl alcohol solution; by treatment with the latter, one of the products formed is tetramethyldiamidoazoxybenzene, and this same body is obtained when it is heated with alcoholic *p*-nitrosodimethylaniline hydrochloride or when *p*-nitrosodimethylaniline itself is heated for a considerable time with alcoholic ethylene dibromide. Its chloroform solution gives a heavy black precipitate with a chloroform solution of iodine, and a rather gelatinous brown precipitate is given by a solution of bromine in chloroform. With very dilute nitric acid the body is broken down with the formation of *p*-nitrosodimethylaniline nitrate and a reduction-product, as will be described in another part of this paper.

p-Nitrosodimethylaniline Hydrobromide. — This substance was separated from the reaction-mixture by dissolving out the red ethylene derivative with glacial acetic acid, or better, with chloroform. After several crystallizations from methyl alcohol the substance was obtained in greenish-yellow crystals, somewhat darker in color than the hydrobromide which was prepared directly from the free *p*-nitrosodimethylaniline for comparison. The analyses, and its conversion into the platinum salt and into the free base leave no doubt, however, as to its identity. The body was dried in a desiccator and analyzed:

I. 0.1130 gram substance gave 0.1702 gram CO_2 and 0.0474 gram H_2O.

II. 0.1801 gram substance gave 19.9 cc. moist nitrogen at 17° C. and 743 mm. pressure.

III. 0.1303 gram substance gave 14.6 cc. N at 19°.25 C. and 742 mm. pressure.

IV. 0.1625 gram substance gave 0.1355 gram AgBr.

V. 0.1545 gram substance gave 0.1276 gram AgBr.

	Calculated for $C_6H_4NO.N(CH_3)_2HBr.$	I.	II.	Found. III.	IV.	V.
C	41.56	41.08	....	....	....	....
H	4.76	4.60	....	....	....	....
N	12.12	....	12.54	12.58	....	....
Br	34.72	....	....	....	35.48	35.14

Chlorplatinate.—For its further identification, the hydrobromide of the nitrosodimethylaniline, the analysis of which is given above, was treated with an excess of chlorplatinic acid dissolved in methyl alcohol. After allowing it to stand over night the crystalline precipitate was collected on a filter, washed with methyl alcohol and ether, and dried, in one case in the air and a vacuum desiccator, and in the second at 85° to 90° C. The analyses show the body to be the chlorplatinate of *p*-nitrosodimethylaniline.

I. 0.1478 gram salt gave, on ignition, 0.0406 gram Pt.

II. 0.1191 gram salt gave, on ignition, 0.0329 gram Pt.

	Calculated for $(NOC_6H_4N(CH_3)_2HCl)_2PtCl_4.$	I.	Found. II.
Pt	27.46	27.47	27.62

This is the same as the body which was obtained by the action of platinic chloride in methyl alcohol solution on the hydrochloride of nitrosodimethylaniline when dissolved in methyl alcohol, but it seems to be different from the platinum salts obtained by Schraube,[1] who mentions two salts, one having the formula $C_{16}H_{20}N_4O_2HCl(PtCl_4) + H_2O$, and the other $C_{16}H_{20}N_4O.2PtCl_4 + H_2O$, which were obtained from dilute acid solution of the hydrochloride by adding platinic chloride in greater or less excess. When a great excess was added he obtained the second salt.

When chlorplatinic acid dissolved in methyl alcohol was added to a methyl alcohol solution of the hydrochloride of *p*-nitrosodimethylaniline the same platinum salt as described above was obtained.

To 1 gram hydrochloride of *p*-nitrosodimethylaniline dissolved in hot methyl alcohol 2.5 grams platinic chloride dis-

[1] Ber. d. chem. Ges., 8, 616.

solved in methyl alcohol were added. A yellowish precipitate fell immediately, and the mixture was heated for a short time. This was collected on a filter, washed with methyl alcohol and ether, and dried for a short time at 90° C. The salt had a deep orange-red color. An analysis gave the following results:

0.3230 gram salt gave 0.0884 gram Pt on ignition.

	Calculated for $(NO.C_6H_4N(CH_3)_2HCl)_2PtCl_4$.	Found.
Pt	27.46	27.37

The filtrate, on standing, deposited well-shaped, deep-garnet crystals. These, on analysis, showed the same percentage of platinum:

0.0962 gram substance gave 0.0263 gram Pt, or 27.34 per cent.

Paranitrosodimethylaniline Hydrobromide.—This salt was also prepared directly by the addition of an aqueous solution of hydrobromic acid to *p*-nitrosodimethylaniline dissolved in methyl alcohol. A bright-yellow body crystallized out, which was collected on a filter, washed with alcohol, and dried in a vacuum desiccator over calcium chloride. On heating to 207° the salt decomposed.

0.1203 gram salt gave 0.0971 gram AgBr.

	Calculated for $NO.C_6H_4N(CH_3)_2HBr$.	Found.
Br	34.63	34.34

The same platinum salt as described above was obtained from this preparation of the hydrobromide. Before analysis it was crystallized from boiling water, washed with alcohol and ether, and dried at about 95° C.

0.1820 gram salt gave, on ignition, 0.0497 gram Pt.

	Calculated for $(NO.C_6H_4N(CH_3)_2HCl)_2PtCl_4$.	Found.
Pt	27.46	27.30

Action of an Alcoholic Solution of Ethylene Dibromide on Paranitrosodimethylaniline.

When *p*-nitrosodimethylaniline is added to an alcoholic solution of ethylene dibromide, and the mixture is heated to boiling for some time, the red ethylene derivative first formed

is decomposed and the nitroso groups are partially reduced, and tetramethyldiamidoazoxybenzene is formed. Eight grams *p*-nitrosodimethylaniline, 18 grams ethylene dibromide, and 30 cc. alcohol (85 per cent), were heated on the steam-bath in a flask attached to a return-condenser for about one and one-fourth hours. The alcohol was then partly distilled off, the residue was allowed to cool, collected on a filter, washed with alcohol, and with sodium hydroxide and alcohol. The greenish-yellow product, crystallized from toluene, melted at 238° to 239° C. It dissolved in dilute sulphuric acid with a red color, and was precipitated as a bright yellow substance by sodium hydroxide. On reduction it gave dimethyl-*p*-phenylenediamine, which was identified by the methylene-blue reaction and isolation of the free base, which, after crystallization from benzene and ligroin, was obtained as colorless needles, melting at about 40° C.

The yield of the tetramethyldiamidoazoxybenzene was 3.1 grams. Analysis gave the following results:

I. 0.1184 gram substance gave 0.2975 gram CO_2 and 0.0815 gram H_2O.

II. 0.1580 gram substance gave 29.7 cc. N at 22°.5 C. and 744.5 mm. pressure.

	Calculated for $C_{16}H_{20}N_4O$.	I.	II.
		Found.	
C	67.60	68.52	....
H	7.04	7.65	....
N	19.72	....	20.79

If the alcoholic solution of ethylene dibromide and *p*-nitroso-dimethylaniline is heated for only a short time, the conversion into tetramethyldiamidoazoxybenzene is by no means complete, and the red crystals of the diparanitrosodimethyl-anilineethylene may be seen in the reaction-mixture, especially after the hydrobromide has been removed by alcohol and sodium hydroxide.

When the red ethylene derivative itself is acted upon by the hydrochloride of *p*-nitrosodimethylaniline in boiling alcohol it is decomposed and the nitroso groups are reduced, just as above, to tetramethyldiamidoazoxybenzene.

Action of Acids on Diparanitrosodimethylanilineethylene.—
This base dissolves easily in both dilute hydrochloric and
sulphuric acids, but by neutralization with either sodium hy-
droxide or sodium carbonate it was impossible to obtain the origi-
nal body again, and as yet no product of the action of these acids
has been isolated and identified. With dilute nitric acid the
reaction seems to go more smoothly, as will be described be-
low. With picric acid in chloroform solution, which offered
no opportunity for hydrolysis, a picrate was obtained.

To 5 grams of diparanitrosodimethylanilineethylene dis-
solved in chloroform, 8 grams of picric acid dissolved in chlo-
roform were added. The solution at first turned purple, and
then yellow crystals separated which were collected on a fil-
ter and washed with a very little chloroform, and finally with
ether. The salt was freed from the solvent by allowing it to
stand in the air, and finally in a desiccator over calcium
chloride and paraffin. On long standing the salt shows a
tendency to change from yellow to light-green on its surface.
The salt gave the following result on analysis:

0.1040 gram substance gave 16.8 cc. N at 23° C. and 756.9
mm. pressure.

	Calculated for $[C_6H_4NO.N(CH_3)_2]_2C_2H_2.(C_6H_2(NO_2)_3OH)_2.$	Found.
N	17.86	18.13

A sample of the salt that had stood in the desiccator so long
that it changed partially in color was also analyzed, but with
the same result.

0.1616 gram substance gave 26.0 cc. N at 755.4 and 18° C.,
which corresponds to 18.47 per cent N.

The body is evidently the neutral diparanitrosodimethyl-
anilineethylene picràte.

Properties of Picric Acid Salt.—This salt melts with decom-
position at about 155° C. It is somewhat soluble in chloro-
form in the cold, giving a yellow solution, but only very
slightly soluble in ether; in hot alcohol it dissolves with a
red color, due to dissociation into the red base and free picric
acid, and with warm water the free diparanitrosodimethylani-
lineethylene separates out as an insoluble body, the picric acid
remaining dissolved. With a dilute solution of sodium hy-

droxide in the cold, the original base was separated from its salt, collected on a filter, and washed with water. It melted with decomposition at 225° without recrystallization.

Picric Acid Salt of Paranitrosodimethylaniline.—This salt was obtained by Schraube,[1] but it was not analyzed, neither were its properties given.

It is obtained as a yellow precipitate when 3 grams of picric acid dissolved in cold benzene are added to 2 grams *p*-nitrosodimethylaniline also dissolved in benzene. This was collected on a filter, washed with benzene, and allowed to dry in the air. After crystallizing from hot water and washing with alcohol, it was dried on a clay plate and finally in a desiccator over calcium chloride to constant weight. The following analytical results were obtained. For the determination of carbon and hydrogen it was found necessary to mix the substance with fine copper oxide.

	Calculated for $NO.C_6H_4N(CH_3)_2.C_6H_2(NO_2)_3OH.$	I.	Found. II.
C	44.32	43.93	....
H	3.43	3.84	....
N	18.47	....	18.62

Properties of Picric Acid Salt of Paranitrosodimethylaniline.— This salt crystallizes from water in rectangular plates. It decomposes at about 140°, showing signs of decomposition below this temperature. It dissolves in cold alcohol with a yellow color, is only slightly soluble in glacial acetic acid and chloroform, still less so in benzene, and is insoluble in ether. It is much more soluble in hot water than in cold. When treated with a sodium carbonate solution and shaken out with ether, the free *p*-nitrosodimethylaniline is obtained.

Action of Dilute Nitric Acid on Diparanitrosodimethylanilineethylene.—As has been mentioned above, this body is broken down when acted upon by mineral acids, even when very dilute. The products formed either by hydrochloric or sulphuric acid have not, as yet, been identified or isolated. With dilute nitric acid, however, the study of the reaction-products is simplified by the fact that one of these, the nitrate of nitrosodimethylaniline, being a much less soluble salt than

[1] Ber. d. chem. Ges., 8, 616.

either the hydrochloride or sulphate, is removed from the solution as soon as formed, while the other products remain in solution.

Five grams of the ethylene derivative were slowly added to 38 cc. of 15 per cent nitric acid diluted with 38 cc. of water. During the addition the mixture was constantly stirred and great pains taken to break up any lumps. The insoluble portion was collected on a filter and washed with a very little nitric acid of the same strength, and was purified by crystallization from a mixture of alcohol and water. After drying at about 95^b C. it was analyzed with the following results :

I. 0.1147 gram substance gave 0.1919 gram CO_2 and 0.0577 gram H_2O.

II. 0.1048 gram substance gave 20.4 cc. N at 25° C. and 763 mm. pressure.

III. 0.1266 gram substance gave 24.4 cc. N at 28° C. and 744 mm. pressure.

	Calculated for $NO.C_6H_4N(CH_3)_2HNO_3$.	I.	Found. II.	III.
C	45.07	45.63	....	....
H	5.16	5.59	....	....
N	19.71	....	20.69	21.64

The body is undoubtedly paranitrosodimethylaniline nitrate, since on treatment with sodium carbonate solution, and shaking out with ether, a green ethereal solution is obtained which deposits crystals melting at 85° to 86° (melting-point of paranitrosodimethylaniline, 85°). It was further identified by comparison with the nitrate made directly from an alcoholic solution of *p*-nitrosodimethylaniline and dilute nitric acid. Both salts melted with decomposition at 162°.

A determination of the nitrogen in the nitrate made directly, gave 20.48 per cent nitrogen.

The filtrate, when made alkaline with sodium carbonate, gave a reddish-yellow precipitate, which, after being washed with alcohol or ether, and crystallized from benzene, or better from alcohol, was obtained in the form of yellow plates (from alcohol), melting at 255° to 256°. This body dissolves with great ease in dilute mineral acids, giving a practically colorless solution, but in glacial acetic acid it dissolves with a blue

color. Extremely dilute chloroform solutions of bromine and chlorine color its chloroform solution a beautiful deep-blue. It seems to contain no oxygen. The study of this body is being continued with others in this laboratory.

The filtrate from this yellow body was allowed to stand for some time, when a further precipitation occurred. This precipitate was filtered off and the alkaline filtrate, after shaking out with chloroform to remove the last traces of the yellow body, was examined. The almost colorless solution decolorized a mixture of potassium permanganate and dilute sulphuric acid, but gave no test for oxalates with calcium salts. It gave negative results for formic aldehyde with a decolorized fuchsin solution. Some of the solution was evaporated to dryness, the residue dissolved in dilute acetic acid, and tested for formic acid. It reduced silver nitrate easily on warming. The presence of formic acid was confirmed by the reddish precipitate given by another part of the solution which had been neutralized with dilute sulphuric acid and heated with ferric chloride, and by the precipitate of mercurous chloride given by heating with a solution of mercuric chloride.

I wish to express my gratitude to Mr. C. W. Whitney for his valuable assistance in a portion of the experimental work described in the first part of this paper.

XCVII.—ON THE MOLECULAR REARRANGEMENT OF THIOCYANACETANILIDES INTO LABILE PSEUDOTHIOHYDANTOÏNS; AND, ON THE MOLECULAR REARRANGEMENT OF THE LATTER INTO STABLE ISOMERS.

By Henry L. Wheeler and Treat B. Johnson.

Theory would require the existence of a large number of isomeric nitrogen-monosubstituted pseudothiohydantoïns, if mono-, bi-, and tricyclo combinations are considered, as well as stereoisomeric forms. But those chemists who have prepared these substances have invariably obtained, or recognized, only one form, even when methods have been em-

ployed which should yield isomers. In this and other respects the pseudothiohydantoïns behave in a tautomeric manner, and, therefore, the question of their structure has not been settled.

P. Meyer obtained phenylpseudothiohydantoïn not only from chloracetanilide and thiourea, but also from ethyl chloracetate and phenylthiourea, and from phenylthiohydantoic acid by warming with acetic acid.[1] He found that it gave N-phenyl-α,μ,diketotetrahydrothiazole (formula V.) when boiled with hydrochloric acid, and, therefore, he assigned the structure represented by formula I. to this compound. He also prepared the corresponding p-tolyl derivative.

$$
\begin{array}{cc}
\text{CH}_2\text{—S} & \text{CH}_2\text{—S} \\
| \quad\quad | & | \quad\quad | \\
\text{CO} \quad \text{C=NH} & \text{CO} \quad \text{C=NC}_6\text{H}_5 \\
\diagdown\diagup & \diagdown\diagup \\
\text{NC}_6\text{H}_5 & \text{NH} \\
\text{I.} & \text{II.}
\end{array}
$$
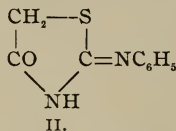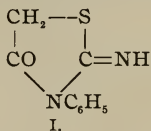
Liebermann and Lange[2] then stated that monoalkylpseudothiohydantoïns might occur in two isomeric forms, formulas I. and II.; but on account of the formation of Meyer's thiohydantoïn from chloracetanilide he assumed that formula I. is correct. Soon after this Andreasch[3] prepared the same substance from phenylcyanamide and thioglycolic acid. He also concluded that of the two forms formula I. is the only one that can represent the structure of the compound. He assigned to the methyl and allyl derivatives a similar constitution.

This structure for phenyl and analogous pseudothiohydantoïns seems to have been accepted without question for fifteen years. To be sure, Neubert[4] gave to the phenylethyl analogue the form represented by formula II., and Goldschmidt and Gessner[5] also viewed the cumyl compound in a similar manner; nevertheless, no evidence in favor of this latter structure was offered.

[1] Ber. d. chem. Ges., **10**, 1965 (1877); **14**, 1661 (1881).
[2] Ann. Chem. (Liebig), **207**, 129 (1881).
[3] Ber. d. chem. Ges., **15**, 325 (1882); Monatsh. Chem., **2**, 776 (1882); **6**, 840 (1885).
[4] Ber. d. chem. Ges., **19**, 1823 (1886).
[5] *Ibid.*, **22**, 933 (1889).

Finally, Dixon,[1] with the object of preparing isomeric pseudothiohydantoïns, investigated the action of chloracetylthiocarbimide on aniline, toluidine, etc. He found, however, that the same substances were formed by this as by other methods. He stated that ''there can be no doubt that one thiohydantoïn alone is the product of interaction between (*a*) monosubstituted thiourea and ethylic chloracetate, (*b*) thiourea and substituted chloracetamide, (*c*) chlorinated acidic thiocarbimide and organic base.'' An experiment also showed that the same compound was formed by boiling thiohydantoïn with aniline.

He then examined the behavior of phenylthiohydantoïn with carbon bisulphide at a high temperature, and found that rhodanic acid (III.) was formed. This was the first evidence produced in favor of formula II. for phenylthiohydantoïn and its analogues. Dixon states that the reaction took place as follows :

$$\begin{array}{cc} \underset{\displaystyle \overset{\displaystyle CH_2 — S}{\underset{\displaystyle NH}{CO \quad C}}=NC_6H_5 + CS_2 = & \underset{\displaystyle \overset{\displaystyle CH_2 — S}{\underset{\displaystyle NH}{CO \quad CS}} + C_6H_5NCS. \end{array}$$

III.
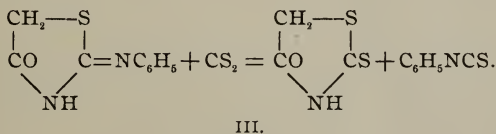
This, however, did not settle the structure of the compounds in question, since it left unexplained not only the formation of N-phenyl-α,μ-diketotetrahydrothiazole (formula V. below) by boiling with hydrochloric acid, but also the fact that isomers are not obtained by other methods, especially that of Andreasch, the synthesis from thiourea and substituted chloracetamide, and the fact that it can be prepared from thiocyanacetanilide by boiling with alcohol.

Rizzo[2] stated that chloracetanilide and ammonium thiocyanate give thiocyanacetanilide, $NCSCH_2CONHC_6H_5$, melting at 176°, but Frerichs and Beckurts[3] found this compound to be the long-known phenylthiohydantoïn of P. Meyer.

Meanwhile, W. Grothe[4] had just described a series of com-

[1] J. Chem. Soc. (London), **71**, 620 (1897).
[2] Centrbl.. 1898, II., 296.
[3] Arch. Pharm., **238**, 615 (1900).
[4] *Ibid.*, **238**, 610 (1900).

pounds which he believed were normal thiocyanacetanilides. Frerichs and Beckurts repeated the work and concluded that by the action of potassium thiocyanate on chloracetanilide there first results the rhodanacetanilide described by Grothe as melting at 86° to 87°. On heating an alcoholic solution of this rhodanide, they found that Meyer's phenylthiohydantoïn was produced.

The latter authors then undertook the examination of Grothe's compounds, in order to determine whether they are normal or isothiocyanates. They believed their results to show that, with the exception of rhodanacetmethylanilide, the substances are normal thiocyanates. Then followed the description of an interesting experiment which was, however, incorrectly interpreted. They stated, but without producing any proof for the structure of the compounds, that when potassium thiocyanate acts on chloracetparatoluide, in alcoholic solution, for only a short time, a labile compound results, which they considered to be isothiocyanacettoluide,

$$SCN—CH_2CONHC_6H_4CH_3.$$

They observed that when this solution was warmed the compound was rapidly converted into a substance which they supposed was normal thiocyanacettoluide,

$$NCSCH_2CONHC_6H_4CH_3,$$

and the latter was finally changed into paratolylthiohydantoïn. This brings us to the point where our work commenced.

We first found that the structure of phenylpseudothiohydantoïn cannot be determined by boiling the compound with hydrochloric acid. Not only is N-phenyl-α,μ-diketotetrahydrothiazole (V.)[1] formed but also α,μ-diketotetrahydrothiazole ("Senfoelessigsäure," formula VI.), which latter substance has been overlooked by previous workers.

CH$_2$——S	CH$_2$——S
CO CO	CO CO
NC$_6$H$_5$	NH
V.	VI.

$$\underset{\text{IV.}}{\underset{HN}{\overset{C_6H_5NH}{>}}CSCH_2COOH}$$
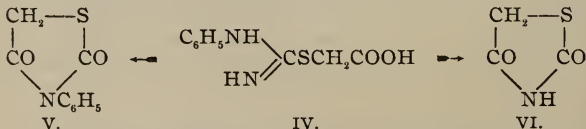
[1] That formula V., represents the structure of this compound and not that assumed by Dixon was shown by Wheeler and Barnes: This JOURNAL, **24**, 64 (1900).

Under this treatment, therefore, the compound behaves in a tautomeric manner. This is undoubtedly to be explained by the assumption that a saponification of the cyclic amide takes place, phenylthiohydantoic acid (IV.) is first formed, and this then condenses and decomposes with the above results.

In view of the fact that the pseudothiohydantoïns are cyclo-acylpseudothioureas, the same molecular rearrangement should be met with in this series as in the corresponding acyclic cases.

In a previous article[1] it has been shown by us that unsymmetrical acetylphenylpseudothioureas, as well as the corresponding acylthioureas, readily undergo a metastatic change into the symmetrical derivatives, as follows:

$$\begin{array}{ccc} \text{CH}_3 & \text{SR} \\ | & | \\ \text{CO} & \text{C}=\text{NH} \\ \diagdown & \diagup \\ & \text{NC}_6\text{H}_5 \\ & \text{VII.} \end{array} \quad \longrightarrow \quad \begin{array}{ccc} \text{CH}_3 & \text{SR} \\ | & | \\ \text{CO} & \text{C}=\text{NC}_6\text{H}_5 \\ \diagdown & \diagup \\ & \text{NH} \\ & \text{VIII.} \end{array}$$

On comparing these structures with those represented by formulas I. and II., it will be noticed that Meyer's structure I. corresponds to the labile acyclic form VII., while the formula of Dixon is analogous to the acyclic stable acetylphenyl-pseudothiourea (VIII.).

Since we found, in our previous work, that the labile acyl-pseudothioureas are too unstable to be crystallized from alcohol without undergoing a molecular rearrangement, the observations of Frerichs and Beckurts seemed to point to a similar state of affairs in the case of the thiohydantoïns. Moreover, it was shown by Wheeler and Merriam[2] that rhodan-acetmethylanilide, contrary to the statement of Frerichs and Beckurts, is not an isothiocyanate. This rendered doubtful the correctness of their assertion that rhodanacet-paratoluide first gives an isothiocyanate. It also seemed highly improbable that normal thiocyanacetanilide undergoes a direct molecular rearrangement into the stable hydantoïn of Dixon, without first forming a hydantoïn having the struc-

[1] This JOURNAL, **27**, 270 (1902).
[2] J. Am. Chem. Soc., **23**, 297 (1901).

ture suggested by Meyer and others. We therefore undertook the preparation of rhodanacetanilides according to Grothe's directions, and were not unprepared for the interesting results which followed.

In the first place, we found that although the phenyl, the orthotolyl, and the paraxylyl compounds are correctly described as rhodanides, on the other hand, the so-called rhodanacetparatoluide and rhodanacetparaphenetidide are neither normal nor isothiocyanates. The paratolyl compound is, in fact, a representative of the missing labile pseudothiohydantoïns, which, for the present, can be represented by Meyer's formula (I.). Dixon's formula (II.), on the other hand, is to be assigned to the long-known phenylthiohydantoïn, a similar one to Grothe's rhodanacetparaphenetidide and to the stable thiohydantoïns previously obtained.[1]

In the second place, the molecular rearrangement of thiocyanacetanilide into the stable hydantoïn does not involve an isothiocyanate at any stage, but proceeds precisely as our previous work would indicate.

(*a*) When chloracetanilide and potassium thiocyanate are dissolved in strong alcohol and warmed about a half hour, a mass of colorless prisms, which melt at about 91°, separate on cooling. This, the first substance formed, is normal thiocyanacetanilide (IX.).

(*b*) When the above compound, in the dry state, is melted on the steam-bath for fifteen minutes, it is converted into an isomeric substance. This melts at 148° and can be crystallized repeatedly from benzene and also from strong alcohol. It is the missing phenylpseudothiohydantoïn (X.).

(*c*) When the above labile products are heated much longer than fifteen minutes on the steam-bath, or for a few minutes at a higher temperature, or boiled for a short time with dilute alcohol, they are transformed, with partial decomposition, into the stable hydantoïn of P. Meyer and others, melting at 178° (XI.).

---

[1] Those pseudothiohydantoïns with the aliphatic groups, methyl and allyl, may be exceptions. In all probability, however, the formulas given to the thiohydantoïns from rhodanacetylthioureas and rhodanacetylurethane (Arch. Pharm., **238**, 319 (1900)) should be revised. This subject will receive attention at a later time.

We have also obtained each of the three products directly, by boiling alcoholic solutions of chloracetanilide and potassium thiocyanate under slightly different conditions, and we have prepared the corresponding ortho- and paratolyl and paraxylyl derivatives. The low temperature, less than 100°, at which the metastatic changes can be produced, is noteworthy.

$$
\begin{array}{ccccc}
CH_2SCN & & CH_2\!-\!S & & CH_2\!-\!S \\
| & & | \quad\; | & & | \quad\; | \\
CO & \rightarrowtail & CO \quad C\!=\!NH & \rightarrowtail & CO \quad C\!=\!NC_6H_5 \\
\searrow & & \searrow\!\swarrow & & \searrow\!\swarrow \\
NHC_6H_5 & & NC_6H_5 & & NH \\
\text{M. P. 91°.} & & \text{M. P. 148°.} & & \text{M. P. 178°.} \\
\text{IX.} & & \text{X.} & & \text{XI.}
\end{array}
$$
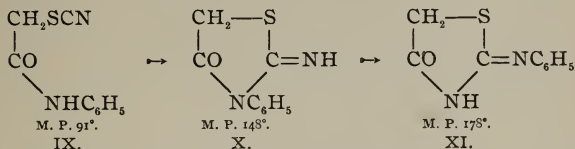
The facts on which the above statements in regard to the structure of the three products are based are as follows:

(*a*) The material melting at 91° was shown to be a normal thiocyanate by warming it in benzene with thioacetic acid, whereupon not more than traces of hydrogen sulphide were given off and a thiol ester was obtained, namely,

$$CH_3CO.SCH_2CONHC_6H_5.$$

There can be no doubt as to the structure of this compound, since we have also prepared it from sodium thioacetate and chloracetanilide.

(*b*) The compound melting at 148°, on treating as above with thioacetic acid, evolved hydrogen sulphide and an acetyl derivative resulted. This behavior towards thioacetic acid shows that the substance is neither a normal nor an isothiocyanate, and since it appears to be the first condensation-product of thiocyanacetanilide it can be represented by formula X.

The possibility must also be considered that this labile compound is a derivative of the unknown furothiole ring (XII.). The condensation would then involve the pseudoform of the anilide as follows:

$$
C_6H_5N\!=\!C(OH)\!-\!CH_2SCN \;\rightarrowtail\; C_6H_5N\!=\!C\!\!\underset{O}{\overset{CH_2\!-\!S}{\diagup\!\!\!\diagdown}}\!\!C\!=\!NH
$$

XII.
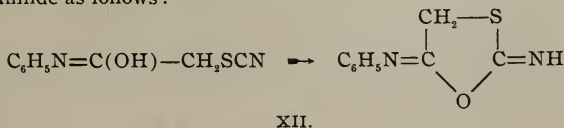
These latter structures, however, for the labile products are excluded, since they are not reconcilable with the ease with which the labile hydantoïns are decomposed into hydantoic acids and substituted cyanamides (see below). This behavior also excludes the possibility that this type of thiohydantoïns has an isomeric structure similar to the isothiohydantoïn of Miolati,[1] which would result if the condensation was analogous to that of the rhodanacetones[2] or to that of orthocyanbenzoic acid.[3]

(*c*) The stable thiohydantoïn has the structure assigned to it by Dixon (formula XI.), because unsymmetrical benzylphenylthiourea,

$$H_2N—CS—N(C_6H_5)CH_2C_6H_5,$$
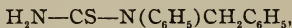
and ethylchloracetate give the same compound as is obtained by treating the stable thiohydantoïn with alkali and benzyl chloride (formula XIII.). This proves that the phenyl group is attached to nitrogen outside the ring, but it does not determine the position of the hydrogen which has been replaced by the benzyl group. If it did, the stable thiohydantoïn would have the structure represented by formula XIV., or some such structure as XV.
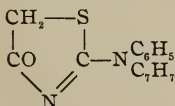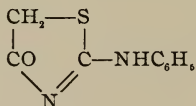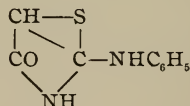
CH_2——S   CH_2——S   CH——S
│   │   │   │   │   ╲ │
CO   C—N⟨C_6H_5 / C_7H_7⟩   CO   C—NHC_6H_6   CO   C—NHC_6H_6
  ╲   ╱╱   ╲   ╱╱   ╲   ╱
   N   N   NH
  XIII.   XIV.   XV.

Formula XIV. represents a compound insoluble in alkali and, therefore, is excluded. Formula XV. is also excluded by the fact that the above benzylphenylthiohydantoïn is insoluble in alkali. The most probable structure for the stable pseudothiohydantoïns is, therefore, that represented by formula XI. This agrees not only with the solubility of the com-

[1] Chem. Centrbl., 1893, I., 641.

[2] Hantzsch and Weber: Ber. d. chem. Ges., **20**, 3127; Arapides: Ann. Chem. (Liebig), **249**, 20.

[3] Sandmeyer: Ber. d. chem. Ges., **18**, 1499; Kuhara: This JOURNAL, **3**, 26; Auger: Ann. chim. phys., [6], **22**, 289; Hoogewerff and Van Dorp: Rec. trav. chim. Pays-Bas, **11**, 91 (1892).

pound in alkali and ammonia but it also corresponds to that structure required for the formation of rhodanic acid. It contains the hydrogen atom in the most probable position, as indicated by the direction[1] of metastatic change in the case of the acylthioureas, and it best explains the fact that the compound is not acetylated by thioacetic acid.[2]

The fact that benzyl chloride gives a compound having the structure represented by formula XIII. is therefore a satisfactory confirmation of the view, expressed several years ago by one of us,[3] that in the alkylation of amidines by means of alkyl halides, the alkyl group does not necessarily directly replace hydrogen, but that in certain cases, if not in general, it unites with a doubly bound nitrogen, $=NR$, in preference. At any rate, the position of hydrogen attached to nitrogen in these cases cannot be determined by alkylation or substitution.[4]

The acetyl derivative mentioned above, which results on warming the labile hydantoïn with thioacetic acid, is identical with the product obtained by the action of acetic anhydride on phenylthiohydantoic acid. It also results when thiocyanacetanilide is warmed with acetic anhydride. From the latter synthesis and the fact that the compound exhibits no tendency to undergo a molecular rearrangement, we conclude that its structure is to be represented by formula XVI. Such an acetyl derivative would be expected from a labile hydantoïn having the structure represented by formula X.

$$
\begin{array}{ccc}
\mathrm{CH_2-\!\!-S} & & \mathrm{CH-\!\!-S} \\
| \quad\quad | & & \| \quad\quad | \\
\mathrm{CO} \quad \mathrm{C}=\mathrm{NCOCH_3} & & \mathrm{HOC} \quad \mathrm{C}=\mathrm{NC_6H_5} \\
\diagdown\;\diagup & & \diagdown\;\diagup \\
\mathrm{NC_6H_5} & & \mathrm{NH} \\
\mathrm{XVI.} & & \mathrm{XVII.}
\end{array}
$$
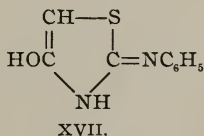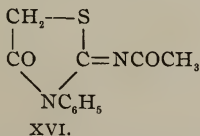
On the other hand, the stable thiohydantoïn, which is not acted on by thioacetic acid, reacts in a peculiar manner with

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[1] This JOURNAL, **27**, 274 (note).

[2] Compare Näf : " On Amidothiazoles," Ann. Chem. (Liebig), **265**, 108 (1891).

[3] This JOURNAL, **20**, 482 (1898).

[4] Compare Knorr : Ber. d. chem. Ges., **28**, 708 (1895) ; Wislicenus : Ann. Chem. (Liebig), **312**, 61 (1900) ; Michael : Ber. d. chem. Ges., **33**, 3740 (1901) ; J. prakt. Chem., **46**, 204 ; **60**, 324 (1899).

acetic anhydride and a diacetyl derivative results. The product is insoluble in cold alkali, and, on warming, the stable thiohydantoïn is recovered. It follows from this that the hydrogen of the methylene group is not directly replaced by one or both acetyl groups. If, as sometimes maintained, the position of hydrogen in tautomeric substances can be determined by acetylation, the structure of the stable thiohydantoïn would therefore be represented by some such formula as XVII., XVIII, XIX., or XX.

$$
\begin{array}{cc}
\text{CH——S} & \text{C——S} \\
\text{HOC} \quad \text{C—NHC}_6\text{H}_5 & \text{HOC} \quad \text{C—NHC}_6\text{H}_5 \\
\text{N} & \text{NH} \\
\text{XVIII.} & \text{XIX.}
\end{array}
$$

$$
\begin{array}{c}
\text{CH——S} \\
\text{N} \\
\text{HOC————C—NHC}_6\text{H}_5 \\
\text{XX.}
\end{array}
$$
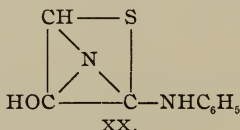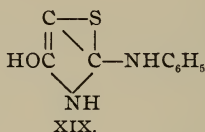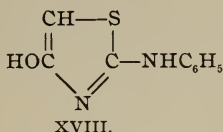
But these formulas are excluded since diphenyl and the above benzylphenylpseudothiohydantoïn are insoluble in alkali. Moreover, Mr. G. S. Jamieson, working in this laboratory, has found that the methylene hydrogen in the stable hydantoïn is capable of reacting with aldehydes and other substances[1] in a similar manner to that of benzyl cyanide.[2] A like behavior had been previously observed by Andreasch in the case of the non-substituted thiohydantoïn,[3] and by others[4] in dealing with compounds which contain the —CO—CH$_2$—S— group.

It follows from these results that acetylation, like alkylation, cannot be relied on to determine the position of hydrogen in the pseudothiohydantoïns.

[1] These reactions will be described in a later paper.

[2] V. Meyer : Ann. Chem. (Liebig), **250**, 124 (1889).

[3] Monatsh. Chem., 8, 407.

[4] Loven . Ber. d. chem. Ges., **18**, 3242 (1885) ; Nencki and Sieber : *Ibid.*, **17**, 2278 (1884) ; Ginsberg and Bondzynski : *Ibid.*, **19**, 119 (1886); Monatsh. Chem., 8, 358 (1887); Andreasch : *Ibid.*, 8, 407, **10**, 75 (1889).

Since in the stable thiohydantoïns the aryl group is outside the ring, it follows also that a corresponding six-membered ring structure described by Langlet[1] as 3-phenyl-2-imino-4-acitetrahydro-1,3-azthin (formula XXI.), prepared from phenylthiourea and β-iodopropionic acid, should undoubtedly be represented by formula XXII. In other words, the compound in question is 2-phenylimino-4-acitetrahydro-1,3-azthin:

$$C_6H_5N \Big\langle \begin{matrix} CO-CH_2 \\ C(NH)S \end{matrix} \Big\rangle CH_2 \qquad HN \Big\langle \begin{matrix} CO-CH_2 \\ C(NC_6H_5)S \end{matrix} \Big\rangle CH_2$$

$$XXI. \qquad\qquad XXII.$$
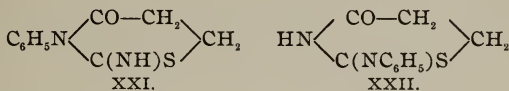
A molecular rearrangement analogous to ours, inasmuch as a cyanogen group and an amido group condense to produce a ring and the resulting compound then undergoes a further rearrangement, was observed by Pschorr[2] in the case of α-arylorthoacetaminocinnamic nitriles. These compounds, under the influence of dilute alkali or acids, are transformed into α-acetamino-β-arylquinolines, the result being expressed as follows:

$$C_6H_4 \Big\langle \begin{matrix} CH=C(CN)R \\ NHCOCH_3 \end{matrix} \quad \longrightarrow \quad C_6H_4 \Big\langle \begin{matrix} CH=CR \\ | \\ N=C-NHCOCH_3 \end{matrix}$$
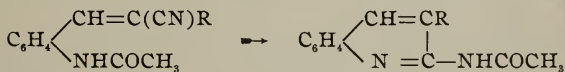
Pschorr and Wolfes state that in this metastatic change no intermediate products could be obtained, and therefore the mechanism was not explained.

In regard to the mechanism of the metastatic changes represented above, by formulas IX., X., and XI., that involved in the first step requires no further consideration. The second molecular rearrangement can be accounted for by the assumption that the labile product (X.) condenses to form a compound having the structure represented below either by formula XXIII. or XXIV. A simple shifting of the bonds, along with hydrogen in the first instance, will then give the structure required by the stable hydantoïn.

[1] Beilstein's Handbuch : Spl. Bd. II., 200 (Privatmittheilung).
[2] Ber. d. chem. Ges., **31**, 1289 (1898) ; Pschorr and Wolfes : *Ibid.*, **32**, 3399 (1899).

XXIII.   XXIV.
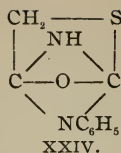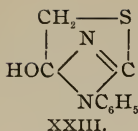
The bicyclo formula (XXIII.) represents an intermediate, inner addition-product, analogous to the intermediate product commonly assumed in the case of the saponification of acid and imino esters by amines,[1] and which was shown by us to exist in the thionurethane series.[2] According to this we have a case of intramolecular saponification similar to Willstätter's "intramolekulare Alkylirung.[3]

A compound having this structure would be analogous to the hypothetical intermediate product by means of which Ransom[4] explains the molecular rearrangement of amino-phenylethyl carbonate into oxyphenylurethane :

$$H_2NC_6H_4O.CO_2C_2H_5 \;\; \rightarrowtail \;\; C_6H_4 \underset{NH}{\overset{O}{<>}} C(OH)OC_2H_5 \;\; \rightarrowtail$$

$$C_2H_5CO_2NHC_6H_4OH.$$
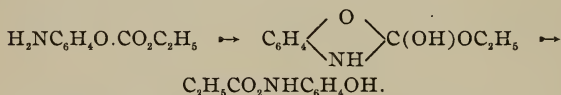
A similar intermediate product may be considered to have at least a momentary existence in the case of the molecular rearrangement of orthoamidobenzylacetparatoluide into ortho-acetamidobenzylparatoluidine, and possibly a like one also during the rearrangement of unsymmetrical diarylsemicarb-azides,[5] although Widman,[6] who described the former change, states that a third product was not observed.

These molecular rearrangements are probably due to the fact that the acyl group has a tendency to migrate to the most positive position in the molecule, and in the above manner the system may avoid a concentration of negative groups.

Formula XXIII. might therefore, without objection, be as-

[1] Stieglitz : This JOURNAL, **21,** 107 (1899).
[2] *Ibid.,* **24,** 191 (1900).
[3] Ber. d. chem. Ges., **34,** 139 (1901).
[4] This JOURNAL, **23,** 11 (1900).
[5] Busch and Holzmann : Ber. d. chem. Ges., **34,** 320 (1901).
[6] J. prakt. Chem., **47,** 354 (1893).

signed to the intermediate product were it not for the interesting, but hitherto unexplained, observation of Walther and Stenz[1] that "phenylparatolylsulfhydantoïn" occurs in two forms, one melting at 113°, the other at 169°, and that the lower-melting substance can be transformed into the higher. Evidently, in this case no such bicyclo combination as XXIII. is possible. If this is actually a molecular rearrangement like ours then the intermediate product can have a tricyclo structure similar to that represented by formula XXIV. In the same manner the reversible molecular rearrangement described by Freund[2] can be explained, in which 1-methyl-2-methylimino-5-thio-3,4-disulphazolidin changes into 2,5-dimethyliminodimethylenetrisulphide and *vice versa*.
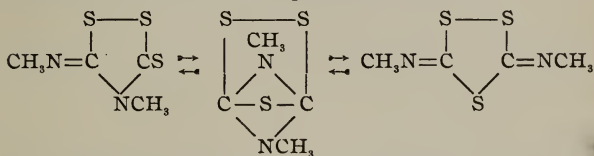
The possibility, however, is not excluded that the mechanism of the molecular rearrangement of disubstituted thiohydantoïns is different from that of the mono derivatives and that the intermediate product in the latter case has the enol structure (XXIII.). Indeed, our experiments do not exclude the possibility that the labile thiohydantoïn itself has this structure. This view receives support from the fact that the labile phenylthiohydantoïn gives a wine-yellow color in the cold with ferric chloride, while the rhodanide and the stable thiohydantoïn do not. Moreover, in the case of the orthotolyl derivatives the labile thiohydantoïn gives the stable isomer on treating with cold alkali, while the thiocyanate, under similar treatment, gives orthotolylcyanamide. In order to give a cyanamide, the rhodanide must first condense to form a compound with the structure represented by formula X., but this is the structure first assigned to the labile hydantoïn. On the other hand, the labile phenylthiohydantoïn and the rhodanide both give phenylthiohydantoïc acid.

[1] J. prakt. Chem., **61**, 576 (1900).
[2] Ann. Chem. (Liebig), **285**, 138 (1895).

This behavior of the labile products with alkali points decidedly to the conclusion that there are three metastatic changes involved in this molecular rearrangement and two structurally different labile thiohydantoïns.   This question and whether the structure of the labile thiohydantoïns that have been isolated is correctly represented by formula X., XXIII., or XXIV. will require further work to decide, and, therefore, we hope to continue the present investigation with especial consideration of these problems at the opening of the next college year.

Either formula XXIII. or XXIV. will explain the mechanism not only of the rearrangement in question, but also that of the acylthioureas, the reaction being a monomolecular one, involving an inner condensation.   In the latter case the intermediate product can be represented by one of the following formulas :
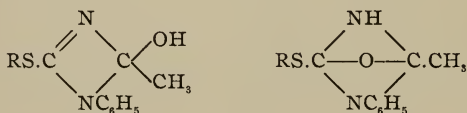
Bicyclo combinations, more or less analogous to XXIII., are now being assigned to a number of compounds. Michaelis[1] advances the formula XXV. for antipyrin[2] and its sulphur and selenium analogues, while Busch has recently obtained a series of substances which, as he believes, have a similar structure.[3]   Interesting in this respect are the corresponding urazole and the isomeric forms of the thiourazoles of Marckwald and Sedlaczek,[4] which, according to Busch,[5] exhibit tautomerism in the sense illustrated by formulas XXVI. and XXVII.   The thiourazoles corresponding to these formulas undergo a reversible rearrangement, as shown by the arrows :

[1] Ann. Chem. (Liebig), **320**, 2 (1902).
[2] A structure previously considered but not accepted by Knorr : *Ibid.*, **293**, 26, (1896).
[3] Ber. d. chem. Ges., **34**, 326 (1901).
[4] *Ibid.*, **29**, 2920 (1896).
[5] *Ibid.*, **35**, 975 (1902).
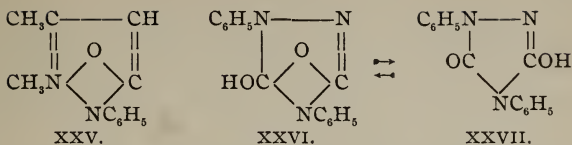
The thiocyanacetanilides and the labile thiohydantoïns, which we have examined, cannot be boiled for any length of time with aqueous alcohol, water, acetic acid, or the like, without more or less readily undergoing decomposition and rearrangement into the stable form. This, and their behavior on heating, explains why the various methods hitherto employed have given only one form of pseudothiohydantoïns. In addition to the above molecular rearrangement, the labile pseudothiohydantoïns readily undergo hydrolysis. A saponification or rupture of the ring takes place immediately on treating with cold alkali, or even on warming for a short time with dilute alcohol.

Three reactions have been observed on treating the thiocyanacetanilides and the labile hydantoïns with cold alkali: (*a*) A molecular rearrangement into the stable form; (*b*) the formation of thiohydantoïc acids; (*c*) a decomposition into substituted cyanamides and thioglycolic acid.

The stable thiohydantoïns, on the other hand, exhibit considerable stability towards alkali, forming crystalline sodium salts, from solutions of which acetic acid precipitates the unaltered material. This fact was observed in the case of stable phenylpseudothiohydantoïn by previous workers.

The behavior of the cyclo derivatives, both with heat and with alkali, is therefore analogous to that of the corresponding acyclic acylthioureas, and it is an interesting fact that the ring structure of the pseudothiohydantoïns confers no especial stability on the labile products and does not interfere with this now general molecular rearrangement.

It can be stated in regard to the ease with which the labile pseudothiohydantoïns undergo molecular rearrangement that they are more closely allied to the labile unsymmetrical acylthioureas than to the labile acylpseudothioureas. The former

acyclic compounds can be easily crystallized from alcohol while the latter cannot, without undergoing a metastatic change. Under certain conditions the labile pseudothiohydantoïns can be crystallized from alcohol, and, in fact, even the thiocyanacetanilides, which are less stable than the labile thiohydantoïns, can be submitted to this treatment.

The homologues of thiocyanacetanilide appear to be more stable than the prototype. However, in all cases care must be taken to avoid prolonged warming, especially in dilute alcohol. Grothe makes no mention of this nor of the formation of thiohydantoïns, thiohydantoic acids, etc. With the exception of rhodanacetparaphenetidide, which was submitted to the violent treatment of being crystallized from acetic acid and consequently gave the stable hydantoïn, all the others were apparently crystallized from dilute alcohol.

In connection with the behavior of our labile compounds with solvents and heat, it is noteworthy that in deciding the identity of products in the case of the amidines, when prepared by methods which should yield isomers, crystallization from alcohol has almost invariably been resorted to before the melting-point of one specimen would coincide exactly with that of the other.[1]

Finally, in concluding this introduction, it must be stated that the molecular rearrangement of the pseudothiohydantoïns and that described by Freund are not the only cases observed in which an alkylimino group within a cyclo structure has been found to undergo a metastatic change to a position outside the ring, or *vice versa*.

Rathke[2] observed a closely analogous case to that of ours among the phenylmelamines, in which the group $=NC_6H_5$ changes places with a $=NH$ group :

$$=\overset{|}{C}-(NC_6H_5)-\overset{|}{C}=NH \quad \rightarrowtail \quad =\overset{|}{C}-NH-\overset{|}{C}=NC_6H_5.$$
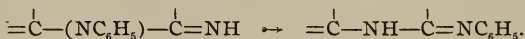
[1] Pechmann : Ber. d. chem. Ges., **28**, 869, 2363 (1895) ; **30**, 1779, 1783 (1897) ; Wheeler and Johnson : *Ibid.*, **32**, 35 (1899). Marckwald, however, describes a case of identical products where neither heat nor alcohol was used (Ann. Chem. (Liebig), **286**, 355 (1895)). Mercaptan, however, was present and the reaction required many days before it was complete. Compare also Hantzsch and Perkin on diazoamino compounds, Ber. d. chem. Ges., **30**, 1394 (1897).

[2] Ber. d. chem. Ges., **21**, 867 (1888).

Pinner[1] found that the normal oxygen hydantoïns, under the influence of alkali, undergo a transformation into pseudo-hydantoïns. In this case an oxygen atom and an imino group shift positions :

$$\overset{|}{R}CH—\overset{|}{N}H—\overset{|}{C}O \;\;\rightharpoonup\;\; \overset{|}{R}CH—O—\overset{|}{C}=NH.$$
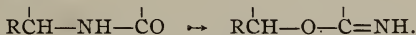
The molecular rearrangement of the isoimides into normal imides described by Hoogewerff and Van Dorp,[2] Van der Meulen,[3] Kuhara and Fukui,[4] is another example of a meta-static change that takes place, in all probability, in a similar manner to that of ours :

$$O\overset{|}{C}—O—\overset{|}{C}=NH \;\;\rightharpoonup\;\; O\overset{|}{C}—NH—\overset{|}{C}O.$$

It is noticeable that in these labile compounds there exists a combination of unsaturated groups, residual affinity or double bonds, the latter usually on each side of a bivalent group. This condition is favorable for a change in the manner in which the atoms are united and therefore significant of the mechanism of these curious molecular rearrangements.[5]

EXPERIMENTAL PART.

The products which we have obtained by boiling alcoholic solutions of potassium thiocyanate with the chloracetanilides have been examined in regard to their behavior towards thiol-acids and alkali, and also on heating. In the case of the orthoxylyl compounds a lack of material rendered it impossible to make a thorough examination. For the same reason rhodanacetphenetidide was not isolated. The reactions have served to determine whether the compounds in question are normal thiocyanates, labile or stable thiohydantoïns, as indicated in the introduction. It need only be further remarked that the action of thioacetic and thiobenzoic acids on this series of rhodanides is by no means as simple as that usually observed in the case of monothiocyanates.[6] It appears that if

[1] Ber. d. chem. Ges., **22**, 686 (1889).

[2] Rec. trav. chim. Pays-Bas., **12**, 12 (1893) ; **13**, 93 (1894).

[3] *Ibid.*, **15**, 282.

[4] This JOURNAL, **26**, 454 (1901).

[5] Compare Lapworth : " On a Possible Basis of Generalization of Intramolecular Changes in Organic Compounds," J. Chem. Soc. (London), **73**, 445 (1898).

[6] J. Am. Chem. Soc., **23**, 283 (1901) ; This JOURNAL, **26**, 345 (1901).

about the calculated quantity of thio acid is used, the conditions are favorable for the formation of a thiol ester; if an excess, either an acetyldithiourethane or a simple dithiourethane results; frequently all three of these compounds. The formation of a simple dithiourethane, which involves the addition of hydrogen sulphide to the rhodanide, has hitherto been observed in this reaction, only in the case of methylene and ethylene rhodanides.[1] In some experiments, on crystallizing the product of the reaction from alcohol, nothing but the stable hydantoïns were obtained. Besides these compounds, more or less sticky varnishes accompany the products, and hydrogen sulphide and cyanogen, or hydrogen cyanide, are evolved. Carbon disulphide was not observed. There are, therefore, no isothiocyanates to be considered.

The melting-, decomposing-, or effervescing-points of the thiohydantoic acids which we describe are not definite. They seem to depend not only on the purity of the sample but also on the rate and manner of heating. In this respect they behave in the same way as phthalic acid and other compounds which decompose or lose water on heating.[2] The melting-points given for these acids are, therefore, only approximate.

Normal Thiocyanacetanilide, $NCSCH_2CONHC_6H_5$. — We have usually obtained this compound when 5 to 10 grams of chloracetanilide were boiled with a slight excess of potassium thiocyanate in 30 cc. of alcohol (95 per cent or absolute), for twenty to thirty minutes. If larger quantities of the chloride are taken it frequently happens that nothing but the labile hydantoïn is obtained. With 30 grams, for example, it is difficult to get the chloride completely acted upon before the formation of the second labile product begins. After the reaction is over, the addition of a little water to the cooled solution causes a mass of fine, colorless, needle-like prisms to separate. These, under the usual conditions of a melting-point determination, melt at about 91°. If slowly heated, they melt below this temperature. On heating very rapidly they have been observed to melt as high as 94°. Nitrogen determinations gave :

[1] Wheeler and Merriam : J. Am. Chem. Soc., **24**, 440 (1902).
[2] Remsen : This JOURNAL, **3**, 30 (1881) ; Wheeler : *Ibid.*, **18**, 830 (1896) ; Baucroft : J. Phys. Chem., **3**, 74 (1899).

	Calculated for $C_9H_8ON_2S$.	Found. I.	II.
N	14.58	14.44	14.64

If an attempt was made to recover the material from the mother-liquors, especially by adding water and then evaporating, a mixture consisting essentially of phenylthiohydantoic acid and the stable thiohydantoïn was obtained. These latter compounds were obtained directly when chloracetanilide and potassium thiocyanate were warmed in dilute alcoholic solution.

When the rhodanide is crystallized from alcohol it forms plates, but the melting-point is lowered to about 86° to 88°. Grothe gives 86° to 87°. When crystallized from benzene, especially if the solutions are dilute, large, thin, transparent plates or scales, like mica, are obtained, which, on exposure to the air, show a decided change in appearance. The first evidence of change begins along the edges of the crystals ; an etching appears, which deepens and spreads until the entire specimen becomes opaque and the colorless material changes to a white mass. The transparent crystals show no sharp melting-point but start to melt at a little above 60° and are completely melted at 83°. At a higher temperature they effervesce explosively. On standing about an hour, however, they melt more sharply at 87° to 88°. It was found that the transparent crystals contain benzene of crystallization, which is rapidly lost on heating or exposure.

The confusing behavior of this substance in regard to melting-point and on crystallizing, together with the fact that in the thioacetic acid reaction various results were obtained, since over four compounds seem to be formed under apparently the same conditions, led us at first to believe that we had to deal with two substances, a rhodanide, melting at about 91°, and a labile thiohydantoïn, melting at 87°. It was only after a number of experiments, in which it was found that similar results could be obtained with a variety of these products, that this view was abandoned.

Action of Thioacetic Acid.—Two grams of the rhodanide, melting at 90° to 91°, and one gram of thioacetic acid in 10 cc. of dry benzene, were heated for two and a half hours on

the steam-bath. The benzene was then removed by evaporation and the residue, washed with dilute sodium hydroxide, was taken up in ether and allowed to crystallize by spontaneous evaporation. On recrystallizing from alcohol colorless, needle-like prisms were obtained which melted at 97° to 98°, and a nitrogen determination agreed with the calculated for acetylthioglycollanilide, $CH_3CO.SCH_2CONHC_6H_5$:

	Calculated for $C_{10}H_{11}O_2NS$.	Found.
N	6.69	6.72

The structure of this compound was established by the fact that the same substance is formed immediately on mixing a warm solution of chloracetanilide in alcohol with sodium thioacetate. When the material thus obtained was mixed with some of the above, it was found that the melting-point was not altered.

Two experiments as above, with thioacetic acid and products melting at about 88°, gave material which, on crystallizing from alcohol, formed the stable hydantoïn.

It happened twice that when 2 grams of the labile product, melting at about 87° and 91°, were heated for two hours in 20 cc. of benzene, with an equal weight of thioacetic acid, that some difficultly soluble material was formed, which crystallized from alcohol in fine, hair-like needles and melted with decomposition at 192°. This product was in all probability an acetyldithiourethane, but there was not obtained a sufficient amount for examination and analysis. The chief product formed in these cases was the thiol ester described above.

In other experiments we obtained the following result: Eight grams of the labile product were heated in 60 cc. of benzene with 7 grams of thioacetic acid for two and a half hours. On cooling then, fine, colorless, crystalline material separated, which formed square plates from alcohol and melted at 162°, showing slight decomposition. Nitrogen and sulphur determinations agreed with the calculated for the dithiourethane, $H_2NCS.SCH_2CONHC_6H_5$:

	Calculated for $C_9H_{10}ON_2S_2$.	Found.
N	12.3	12.1
S	28.3	28.4

In accordance with this, the material dissolves in alkali and suffers decomposition, forming alkali thiocyanate and the sodium salt of thioglycollanilide. Hydrogen chloride precipitates material melting at 107° to 108° (thioglycollanilide[1]).

Action of Alkali.—Both the products melting at 88° and 91° dissolve immediately in cold sodium hydroxide, and carbon dioxide thereupon throws down a colorless crystalline precipitate, practically insoluble in alcohol, which melts at about 185° to 190° with decomposition and effervescence. A nitrogen determination agreed with the calculated for phenylthiohydantoic acid, $C_6H_5N=C(NH_2)SCH_2COOH$:

	Calculated for $C_9H_{10}O_2N_2S$.	Found.
N	13.33	13.41

Behavior on Heating : Labile Phenylpseudothiohydantoïn.— A sample of the rhodanide, which melted at 90° to 91°, was melted in a capillary tube and cooled ; on reheating it showed no signs of melting until the temperature reached 136° to 140°. When larger quantities are melted for a few minutes on the steam-bath, then crystallized from benzene, beautiful, square tables result which melt at 148°, forming a blood-red liquid. When quickly cooled from a mixture of benzene and petroleum ether the material forms acicular crystals. This labile product, unlike the rhodanide, can be repeatedly crystallized from strong alcohol ; however, when boiled with dilute alcohol, phenylthiohydantoic acid and the stable hydantoïn result. The latter is also formed when the labile products are allowed to remain too long at a temperature of 100°. Nitrogen determinations in the case of the tables melting at 148° agreed with the calculated for α-keto-μ-imino-N-phenyltetrahydrothiazole :

	Calculated for $C_9H_8ON_2S$.	Found. I.	Found. II.
N	14.58	14.90	14.42

The crystallography of the labile phenylpseudothiohydantoïn melting at 148° and also that of the stable phenylpseudothiohydantoïn was investigated by Mr. Paul C. Condit under the direction of Professor S. L. Penfield. We take this occa-

[1] Rizzo : Centrbl., 1898, II., 296.

sion to express our thanks for the work. The crystals of the labile phenylpseudothiohydantoïn selected for measurement were obtained by crystallizing the material from strong alcohol. They were transparent, had a pale-yellow color, and looked like cubes, having a diameter of about 2 mm.

Their crystallization, however, is orthorhombic and the forms usually observed were only the prisms, $m = 1,1,0$ and the basal planes, $c = 0,0,1$. In some cases domes occurred, $d = 0,1,1$. The habit is shown in Fig. I. The faces were badly etched, especially the c faces. The character of these etchings on the basal planes, which were parallel to the diagonals, is shown in Fig. II.
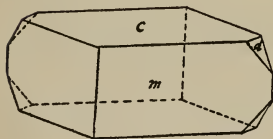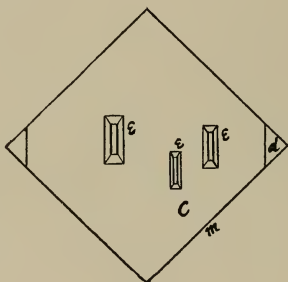
Fig. I. Fig. II.

Many crystals were concave on the upper and lower faces. Owing to the etchings it was not possible to obtain satisfactory measurements from any one crystal, and those given are the average of eleven crystals which gave the most closely agreeing results:

$$m \wedge m' = 87° 44'; \qquad m \wedge m''' = 92° 0';$$
$$d \wedge d' = 53° 12'; \qquad m \wedge c = 90° 0'.$$

The axial ratio is:

$$a : b : c : : 0.97 : 1 : 1.35.$$

In polarized light the crystals showed a bi-axial interference and an extinction direction parallel to the diagonals; the cleavage is also parallel to the diagonals.

The *hydrochloride*, obtained by treating a benzene solution of the labile phenylpseudothiohydantoïn with dry hydrogen chloride, melts with effervescence at 192° to 193°. A nitrogen determination gave :

	Calculated for $C_9H_9ON_2ClS$.	Found.
N	12.25	12.38

The *picrate* separates in bright-yellow prisms from alcohol and melts at 180°.

Action of Thioacetic Acid.—When the material melting at 148° was warmed in benzene with thioacetic acid, hydrogen sulphide was evolved in quantity. The product was then crystallized from alcohol, whereupon colorless, needle-like prisms were obtained, which melted at 191° to 192°. We also prepared this acetyl derivative by three other methods, namely, by the action of acetic anhydride on both of the labile products and on phenylthiohydantoic acid. The rhodanide readily dissolves in cold acetic anhydride while the labile hydantoïn does not, and to effect acetylation it is necessary to warm the solutions in both cases for some time on the water-bath. A nitrogen determination gave results agreeing with the calculated for α-keto-μ-acetimido-N-phenyltetrahydro-thiazole :

	Calculated for $C_{11}H_{10}O_2N_2S$.	Found.
N	11.96	12.00

Action of Alkali.—The labile phenylthiohydantoïn dissolves in cold sodium hydroxide to form a light-yellow solution, from which carbon dioxide precipitates phenylthiohydantoic acid.

Behavior on Heating : Stable Phenylpseudothiohydantoïn.—When the labile hydantoïn melting at 148° is melted in a capillary tube and heated to 165° the material undergoes the next metastatic change, since, when cooled and reheated, it melts at a higher temperature. The transformation of the above labile compounds, and also their analogues, into the stable hydantoïn, by heat, is invariably accompanied by more or less decomposition. The material assumes a reddish-brown color, even when the change is produced by prolonged heat-

ing at 100°. In this case, if the temperature does not exceed 150° to 155°, the decomposition-products are easily extracted by boiling with benzene, and pure phenylpseudothiohydantoïn is left as a difficultly soluble residue, melting at 178°.

It is noteworthy that while the stability of the compounds in this series increases from the rhodanide to the stable hydantoïn, the solubility diminishes. For the preparation of the stable hydantoïns in quantity, the method of P. Meyer, which consists in boiling the hydantoïc acids with acetic acid, is most convenient.

The crystals of the stable phenylthiohydantoïn belong to the triclinic system. Those obtained for measurement were about 2 mm. in length and were formed in alcoholic solution. The forms observed were $a = 0,1,0$; $b = 1,0,0$; $c = 0,0,1$; $d = 1,0,1$; $M = 1,1,0$. The majority of crystals showed only the pinacoids, a and b, and the dome, d. The habit is shown in Figs. III. and IV.
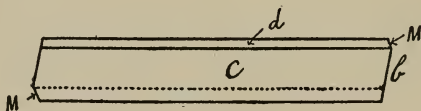
Fig. III.

Nearly all the crystals were twinned in a complicated manner and it was not possible to obtain any satisfactory results under the microscope. The average results of many measurements were as follows :

$$a \wedge b \;\; 78° 51'; \qquad b \wedge c \;\; 77° 53'; \qquad a \wedge c \; 64° 56';$$
$$a \wedge d \; 108° 52'; \qquad b \wedge m \; 39° 33'.$$

From this

$$\alpha = 108° 25'; \qquad \beta = 113° 15'; \qquad \gamma = 96° 35'.$$

The axial ratio is :

$$a : b : c : : \; 1.508 : 1 : 0.859.$$

The crystals showed a cleavage parallel to the base.
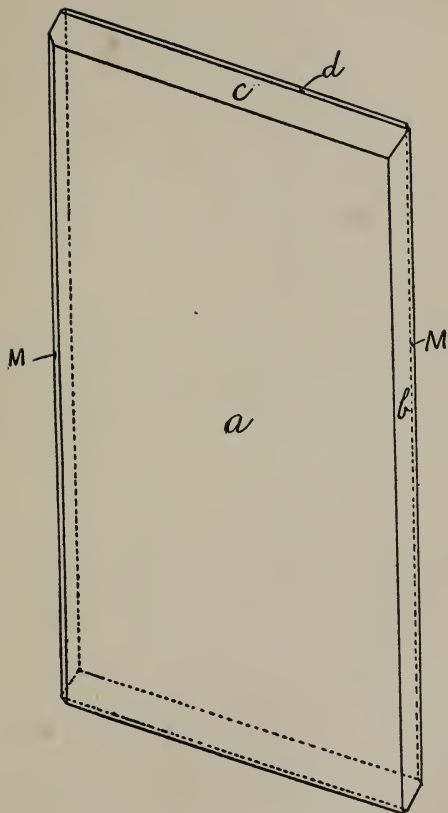
Fig. IV.

Action of Acetic Anhydride.—No reaction was observed to take place when the stable phenylpseudothiohydantoïn was heated with thioacetic acid in boiling benzene. When it was dissolved in acetic anhydride and warmed for a few hours on the steam-bath, a solution resulted which deposited no crystals on cooling. The addition of water then produced a precipitate which crystallized from benzene in flat prisms and melted at 161° to 162°. When mixed with the above acetyl derivative, melting at 163°, which was obtained from the labile monocyclohydantoïn and thioacetic acid, the melting-point was lowered to 135° or 140°. Nitrogen determinations agreed with the calculated for a diacetyl derivative:

	Calculated for $C_{13}H_{12}O_3N_2S$.	I.	Found. II.	III.
N	10.1	10.3	10.2	10.0

This compound is insoluble in cold dilute alkali, but on warming it dissolves and acetic acid precipitates the stable hydantoïn. Quantitative determinations of the acetyl groups were made by boiling the material with standard potassium hydroxide and then titrating the excess of alkali with hydrochloric acid.

Calculated for (CH_3CO-).	Calculated for $(CH_3CO-)_2$.	Found. I.	II.
18.3	31.1	35.4	35.0

This diacetyl derivative was also obtained by warming the stable hydantoïn in benzene with an excess of acetyl chloride (Analysis III. above). Under these conditions the hydrochloride of the hydantoïn is also obtained.

The *stable phenylpseudothiohydantoïn hydrochloride* can be crystallized from alcohol. It then forms colorless needles which melt at 203° with decomposition and effervescence. It is insoluble in benzene.

Action of Alkali and Benzyl Chloride.—When the stable hydantoïn is treated with dilute sodium hydroxide it dissolves, and suddenly a mass of colorless plates of the sodium salt separate. This can be crystallized from boiling water. Carbon dioxide or acetic acid then liberates the unaltered hydantoïn. Five and a half grams of the stable hydantoïn were

warmed on the steam-bath with the calculated quantity of sodium dissolved in dilute alcohol and a slight excess of benzyl chloride. After the alkaline reaction had disappeared the alcohol was evaporated and the residue, when washed with alkali, taken up in ether, and crystallized from alcohol, gave beautiful square tables which melted at 124° to 125°. The same material was obtained from unsymmetrical benzyl-phenylthiourea, $C_6H_5.CH_2(C_6H_5)N—CS—NH_2$, and ethyl chloracetate by proceeding in the usual manner. The crystals thus obtained had the same melting-point as the above and when samples of the two were mixed the melting-point was not lowered. Dixon gives the melting-point of this hydantoïn at 118° to 119° (corr.).

Normal Thiocyanacetorthotoluide, $NCSCH_2CONHC_6H_4CH_3$. —When chloracetorthotoluide was boiled for ten to thirty minutes, in alcoholic solution, with potassium or ammonium thiocyanate, a compound resulted which, on crystallizing from dilute alcohol, formed colorless needles that melted at 102° to 103°, as stated by Grothe. When this material was suspended in ether, in which it is very difficultly soluble, and warmed for two hours, the material, when simply washed, then melted at about 109°. The same effect was produced when the product melting at 102° to 103° was crystallized a number of times from benzene. The long needle-like crystals then had a more prismatic habit. Both these products behaved in the same manner towards thioacetic acid.

Action of Thioacetic Acid.—About 2 grams of the material and 1 gram of thioacetic acid, freshly distilled over phosphorous sulphide, were mixed in 7 cc. of benzene that had been boiled over sodium. The mixture was boiled for one hour, and then, on evaporating the benzene and treating the brown varnish, thus obtained with ether, material separated which proved to be very difficultly soluble in alcohol, and, on boiling, it remained as a sandy, white powder ; a portion separated from the solution in the form of needles. The material melted with effervescence to a deep-brown liquid near 200°. It had all the properties of a dithiourethane, and a nitrogen determination indicated that the substance is an acetyldithiourethane, $CH_3CONHCSSCH_2CONHC_6H_4CH_3$:

	Calculated for $C_{12}H_{14}O_2N_2S_2$.	Found.
N	9.9	10.6

Action of Thiobenzoic Acid.—The material was better characterized as a rhodanide by means of thiobenzoic acid. The treatment was the same as with thioacetic acid. Colorless or pale-yellow material was obtained which crystallized from alcohol in long needles that melted at about 141° to 142°. A nitrogen determination showed that this is benzoylthioglycoll-orthotoluide, $C_6H_5.CO.SCH_2CONHC_6H_4CH_3$:

	Calculated for $C_{16}H_{15}O_2NS$.	Found.
N	4.9	5.41

There can be no doubt in regard to the structure of this compound since we have also prepared the substance from the chloride and potassium thiobenzoate. The material melting at 109° or at 102° to 103° is therefore a normal thiocyanate.

Action of Alkali.—The rhodanide was dissolved in cold alkali and acetic acid then precipitated an oil which readily solidified. On crystallizing from alcohol and ether, in which the material was very soluble, colorless prisms, melting at 77°, were obtained. This material was free from sulphur and proved to be identical with orthotolylcyanamide described by Voltmer.[1]

Behavior on Heating : Labile Orthotolylpseudothiohydantoïn.—Although the rhodanide melts at 109° under the usual conditions of a melting-point determination, and on remelting, practically the same fusing-point is noticed, nevertheless, it can be melted by warming for a half hour on the steam-bath. It then forms a brown tar on cooling. If heated for a sufficient time, crystals of stable orthotolylpseudothiohydantoïn separate. An attempt was made to avoid the formation of this tar by heating in boiling toluene, and for this purpose 3 grams of the material were dissolved in 10 cc. of the solvent and boiled for five minutes; on cooling, unaltered material separated which melted at 109°. On evaporating the toluene on the steam-bath nothing but a brown-black tar and crystals of the stable hydantoïn were obtained.

[1] Ber. d. chem. Ges., **24,** 381.

Finally it was found that a labile product intermediate between the rhodanide melting at 109° and the stable body melting at 144° to 145°, could be prepared as follows, although the yield is poor on account of the formation of decomposition-products. A little over 7 grams of the air-dried rhodanide were heated to 110° in an oil-bath for thirty minutes. During this process a quantity of material sufficient for a melting-point determination sublimed in colorless needles. It melted at 109° and was therefore the unaltered substance. When the brown mass was extracted with benzene about 0.3 gram of an insoluble product was obtained. This melted at 222° with effervescence and proved to be orthotolylthiohydantoic acid. The benzene filtrate, on spontaneous evaporation, deposited small, lozenge-shaped crystals, which were purified by warming with small quantities of benzene. The colorless material thus obtained, about a gram, on rapidly heating in a capillary tube, melted at 131° to 132° and quickly crystallized again, even when the temperature was maintained above 132°. It then refused to melt completely until heated to 142° to 145°. This inter-mediate product appears to be less stable than the correspond-ing phenyl compound. Although it can be crystallized from benzene, nevertheless, on continued warming in this solvent it is converted into the stable hydantoïn. It dissolves on gently warming with dilute alkali, and acetic acid precipitates the stable hydantoïn.

Stable Orthotolylpseudothiohydantoïn, for purposes of com-parison, was prepared from orthotolylthiourea and chloracetic acid. It crystallized in two forms, long needles and stout tables, and both forms melted at 144° to 145° as stated by Dixon, and when mixed with the final product of the above molecular rearrangement, the melting-point was not lowered. In passing, it may be remarked that orthotolylthiourea was observed to melt at 162° and not at 155°, the melting-point given by Staats.[1]

Action of Acetic Anhydride.—When the stable hydantoïn was warmed on the steam-bath with acetic anhydride a solu-tion was obtained from which water precipitated an oil. On standing some time the material solidified, and when crystal-

[1] Ber. d. chem. Ges., **13**, 136 (1880).

lized from alcohol it formed stout, six-sided tables, which melted at 91° to 92°. It is very soluble in benzene and insoluble in cold alkali. The analysis gave results agreeing with the calculated for a diacetyl derivative :

	Calculated for $C_{14}H_{14}O_3N_2S$.	Found.
N	9.66	9.95

Orthotolylthiohydantoic Acid.—This was obtained in one attempt to prepare the labile hydantoïn. Four grams of chloracetorthotoluide and 3 grams of potassium thiocyanate were dissolved in 30 cc. of alcohol and heated for a half hour on the steam-bath. On adding water nothing but a turbidity resulted. The solution was then concentrated, whereupon a colorless, insoluble, white powder separated. It formed small, thin plates and decomposed with effervescence between 208° and 230°. A nitrogen determination gave :

	Calculated for $C_{10}H_{12}O_2N_2S$.	Found.
N	12.50	12.68

On further concentrating the solution stable hydantoïn was obtained.

Normal Thiocyanacetparatoluide, $NCSCH_2CONHC_6H_4CH_3$.— When chloracetparatoluide and potassium thiocyanate are boiled in alcoholic solution for a short time and the mixture that results is crystallized from absolute alcohol or benzene, it forms needle-like prisms and the melting-point of the product appears to be constant at about 85°.

Action of Thioacetic Acid.—The material was heated with thioacetic acid for forty-five minutes in benzene solution. On distilling the benzene and testing for carbon disulphide not a trace was found. The substance, therefore, is not an isothiocyanate. On the other hand, by the Prussian-blue test, hydrogen cyanide was found to be present. The chief product formed, however, was not a thiol ester, but it had all the properties of a dithiourethane. Nitrogen and sulphur determinations agreed with the calculated for the compound $CH_3C_6H_4NHCOCH_2S.SCNH_2$:

	Calculated for $C_{10}H_{12}ON_2S_2$.	Found.
N	11.66	11.92
S	26.66	25.88

Behavior on Heating.—A specimen of the rhodanide, which melted at about 85°, began to solidify at 86°. It was heated a few degrees higher and then cooled. On reheating, it did not melt completely until at about 120°. When the material was melted on the steam-bath for a few minutes and then crystallized from absolute alcohol it formed colorless needles which melted at 125° to 126°, the melting-point previously found for the rhodanide. This latter material is:

Labile Paratolylpseudothiohydantoïn.—This results when the solutions of the chloride and potassium thiocyanate are warmed on the water-bath for a half hour.

Action of Thioacetic Acid.—A portion of the crude labile hydantoïn was warmed in benzene with thioacetic acid. Hydrogen sulphide was evolved in quantity and, on cooling, crystals separated. On crystallizing from alcohol beautiful, colorless plates were obtained which melted at 175° to 176°. That this was neither a thiol ester nor a dithiourethane was shown by the fact that the same acetyl derivative resulted on warming the labile hydantoïn with acetic anhydride. A nitrogen determination gave:

	Calculated for $C_{12}H_{12}O_2N_2S$.	Found.
N	11.29	11.12

Action of Alkali.—The labile hydantoïn dissolved in cold alkali and carbon dioxide, then precipitated a cream-colored, crystalline powder, which was insoluble in water, very difficultly so in alcohol, and which decomposed at about 210° to 212°, with effervescence. A nitrogen determination gave results agreeing with the calculated for paratolylthiohydantoic acid:

	Calculated for $C_{10}H_{12}O_2NS$.	Found.
N	12.50	12.21

Behavior on Heating.—When the material melting at 125° is melted in a capillary tube and cooled it gives a varnish.

If not heated too much or too long it can be solidified and then remelts at 125°. Several grams of the labile hydantoïn, which, after one crystallization from benzene, melted at 121°, were dried and warmed on the steam-bath. In a few minutes the material became colored and in a half hour it was mostly melted. The heating was continued for a half hour longer, whereupon, on cooling, the brown mass readily solidified and an odor of hydrogen cyanide or cyanogen was present. The material was now difficultly soluble in benzene and on simply boiling with this solvent pure, stable paratolylpseudothiohydantoïn, melting at 183°, was left as a residue, while the benzene solution contained the varnish-like impurities that were formed during the metastatic change. When the labile hydantoïn was heated in an oil-bath at temperatures near its melting-point for a short time, a deep-brown mass was obtained, which, on crystallizing from benzene, melted incompletely at about 175°. The question whether this product contains a new isomer or is simply impure stable hydantoïn must be decided later. It is interesting to note also that a change into the stable hydantoïn, accompanied by the formation of a brown coloring-matter, can be brought about in a few hours on exposing this high-melting labile hydantoïn to a temperature as low as 75°.

The *stable paratolylpseudothiohydantoïn*, obtained as above, or by concentrating the aqueous alcoholic filtrates from the labile derivatives, formed needles from alcohol which melted at 183°, as stated by P. Meyer. On treating this material with alkali it was converted into a mass of thin plates or lozenge-shaped spangles of the sodium salt, which, with acetic acid, gave unaltered hydantoïn.

Action of Acetic Anhydride.—The stable hydantoïn was warmed on the water-bath with an excess of acetic anhydride for about an hour and a half. Water then precipitated material which crystallized from alcohol in the form of pale-yellow prisms melting at 163° to 164°. A nitrogen determination gave a result agreeing with the calculated for a diacetyl derivative:

	Calculated for $C_{14}H_{14}O_2N_2S$.	Found.
N	9.66	10.00

Labile α-Orthoxylylpseudothiohydantoïn (?).—The orthoxylidine was prepared by nitrating 50 grams of orthoxylene with a mixture of 50 grams of red fuming and 400 grams of ordinary concentrated nitric acid at 10°. The yield of nitroxylene, boiling at 163° to 173° at 50 mm. pressure, was 25 grams. When the xylene is nitrated with red, fuming[1] nitric acid alone, little or no mononitroxylene is obtained. The nitro compound was reduced with tin and hydrochloric acid in the usual manner. When the chloracetyl derivative of this amine was treated with potassium thiocyanate, as in the case of the phenyl compound, and the product was crystallized from benzene, colorless plates were obtained which, instead of melting at 103° as stated by Grothe, melted at 111°.

Action of Thioacetic Acid.—Three grams of the labile xylylhydantoïn were warmed for about a half hour in benzene with thioacetic acid. The benzene, on evaporating, left a varnish which was washed with water and crystallized from dilute alcohol, whereupon pale-yellow needles were obtained, which melted at 179°. This material was soluble in alkali and was reprecipitated unaltered by acetic acid. A nitrogen determination agreed with the calculated for the stable hydantoïn, α-keto-μ-α-orthoxylyliminotetrahydrothiazole :

	Calculated for $C_{11}H_{12}O_2N_2S$.	Found.
N	12.74	12.81

α-Orthoxylylthiohydantoïc Acid.—On concentrating the filtrates from the preparation of the labile hydantoïn and warming the residue with water, some insoluble, colorless, minutely crystalline material was obtained which was observed to melt at about 208° with effervescence and decomposition. A nitrogen determination gave :

	Calculated for $C_{11}H_{14}O_2N_2S$.	Found.
N	11.76	11.64

[1] Jacobson states fuming acid (Ber. d. chem. Ges., **17**, 160).

Normal Thiocyanacetparaxylidide, $NCSCH_2CONHC_6H_3(CH_3)_2$ $CH_3, NH, CH_3, 1, 2, 4$.—The xylidine employed was isolated from commercial material by means of the excellent method of Hodgkinson and Limpach.[1] The chloracetyl derivative melted at 153°. When this was boiled with potassium thiocyanate for a half hour in alcoholic solution, the crystals that separated melted at 125°–129°. On recrystallizing from alcohol they melted at a lower temperature. From the mother-liquor more was obtained by adding water. This melted less sharply at 118° to 124°, but on drying and crystallizing from benzene it formed colorless plates and melted at 133°, the melting-point previously assigned to this rhodanide. Some of the material melting at 125° to 129° was dissolved in alcohol and evaporated to dryness on the water-bath. It then melted at 120° to 130°. On repeating this treatment it still melted at about 120° to 125°. It was then boiled for two hours in strong alcohol, whereupon, on evaporating to dryness, a thick varnish was obtained from which the stable hydantoïn melting at 161° to 162° separated on treating with benzene.

Action of Thioacetic Acid.—About 2 grams of the material melting at 125° to 129° were heated with a slight excess of thioacetic acid in 10 cc. of benzene for little over an hour. Very little hydrogen sulphide was given off, and on cooling beautiful, colorless prisms separated which, when crystallized from alcohol, melted at 139° to 140°. A nitrogen determination agreed with the calculated for acetylthioglycollparaxylidide, $CH_3CO.SCH_2CONHC_6H_3(CH_3)_2$:

	Calculated for $C_{12}H_{15}O_2NS$.	Found.
N	5.90	5.83

Action of Alkali.—Some of the material melting at 125° to 129° was dissolved in cold, normal sodium hydroxide. Acetic acid then precipitated a colorless, crystalline powder, which formed flat prisms from dilute alcohol and melted, when further purified by recrystallizing from a mixture of benzene and petroleum ether, at 118°. This material was free from sulphur, and nitrogen determinations agreed with the calculated for paraxylylcyanamide, $C_6H_3(CH_3)_2NH—CN$:

[1] J. Chem. Soc. (London), **77**, 65.

	Calculated for $C_9H_{10}N_2$.	I.	Found. II.
N	19.17	18.91	19.16

Behavior on Heating.—Not only is this rhodanide most stable in solvents but also when heated in the dry state. On melting in a capillary tube it forms a varnish. A portion was heated on the steam-bath and it required two hours or more to obtain the material in a completely melted condition. On crystallizing the black varnish thus obtained from benzene a small amount of unaltered rhodanide, which melted at 131° to 133°, was recovered. A slight residue, insoluble in benzene, proved to be paraxylylthiohydantoic acid, while from the benzene solution, on further concentration, crystals of the stable hydantoïn separated.

Labile Paraxylylpseudothiohydantoïn.—The rhodanide was converted into a compound that appears to be the labile hydantoïn by boiling in dry ether for one or two hours. The material remained mostly undissolved, and then, on crystallizing from benzene, beautiful needles separated which melted constantly at 109° to 110°. A nitrogen determination gave:

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
N	12.72	12.84

Action of Thioacetic Acid.—Although the rhodanide reacts readily with thioacetic acid, on the other hand, the labile hydantoïn can be boiled in benzene for hours without giving much evidence of a reaction. After warming more than twenty-four hours the product was a mixture. It melted at 105° to 114° and under the microscope it was seen to consist of needles and prisms. We did not succeed in purifying this material by crystallizing from benzene, and further attempts were abandoned. When the labile hydantoïn is treated with alkali it gives paraxylylcyanamide.

Paraxylylthiohydantoic acid,
$C_6H_3(CH_3)_2N(H_2N)CSCH_2COOH$, was obtained, mixed with brown decomposition-products, when the alcoholic solutions from the rhodanide were diluted with water and evaporated on the steam-bath. It was purified by boiling with alcohol, in which it only partially dissolved. It then decomposed at

about 200° with effervescence. A nitrogen determination gave :

	Calculated for $C_{11}H_{14}O_2N_2S$.	Found.
N	11.76	11.94

When this acid was dissolved in alkali it gave *p*-xylyl-cyanamide.

Stable Paraxylylpseudothiohydantoïn.—The alcoholic extracts from the above hydantoïc acid were evaporated to dryness on the steam-bath. From the brown residue material was obtained which crystallized from a mixture of benzene and petroleum ether in the form of minute prisms, and melted at 161° to 162°. A nitrogen determination gave :

	Calculated for $C_{11}H_{12}ON_2S$.	Found.
N	12.72	12.65

This hydantoïn is quite soluble in alcohol. It dissolves in normal sodium hydroxide and can be precipitated unaltered by carbon dioxide.

The paraphenetidine employed in the following experiments was prepared from paranitrophenetol by reduction with tin and hydrochloric acid. The nitration of phenetol was accomplished by dissolving three parts of the material in a mixture of 2 parts of red, fuming nitric acid and 16 parts of ordinary concentrated nitric acid, the whole being kept at a temperature of 5° to 15°. On diluting with ice-water and washing, the liquid orthonitrophenetol was removed by pressing on a vacuum filter. The paranitrophenetol boiled at 146° at 11 mm. pressure. The rhodanide in this case was not obtained in a pure condition.

Labile Paraphenetylpseudothiohydantoïn.—A crude product, obtained by boiling an alcoholic solution of chloracetpara-phenetidide with potassium thiocyanate for a short time, and which melted at 100° to 115°, was dried and crystallized from benzene. It then melted constantly at 128°. A nitrogen determination gave :

	Calculated for $C_{11}H_{12}O_2N_2S$.	Found.
N	11.8	12.1

Another crude product, melting at 95° to 110°, was suspended in ether and boiled. This procedure gave the same compound, melting at 128°.

Action of Thioacetic Acid.—When the labile hydantoïn was warmed in benzene solution with thioacetic acid, hydrogen sulphide was evolved. The product formed needles or prisms from alcohol and melted at 155°. A nitrogen determination agreed with the calculated for a monoacetyl derivative:

	Calculated for $C_{13}H_{14}O_3N_2S$.	Found.
N	10.00	10.26

Behavior on Heating.—When the labile hydantoïn is melted in a capillary tube and slowly cooled it solidifies. On reheating it shows no signs of melting at 128°, but melts at about 151° to 155° to a deep-red liquid. A portion was melted in an oil-bath at 140° to 145° for about a half hour. Considerable tar was formed and on crystallizing from benzene it melted constantly at 155°, sintering at about 150°. When it was crystallized from dilute acetic acid or dissolved in alkali and precipitated by carbon dioxide, the stable thiohydantoïn was obtained which melted at 163° to 164°. Whether the product melting at 155° is simply impure stable hydantoïn or not must be decided later.

Paraphenetylthiohydantoic Acid was obtained on concentrating the aqueous alcoholic filtrates from the rhodanide and the labile hydantoïn. It separated as an insoluble powder, which, after boiling with alcohol and benzene, decomposed at about 212° with effervescence. A nitrogen determination gave:

	Calculated for $C_{11}H_{14}O_3N_2S$.	Found.
N	11.02	11.08

This acid readily dissolves in dilute alkali, and carbon dioxide precipitates the material unaltered.

Stable Paraphenetylpseudothiohydantoïn was obtained from the alcohol and benzene extracts mentioned above. It was precipitated as a white powder by petroleum ether, and it melted at 163° to 164°. A nitrogen determination gave:

<table>
<tr><th></th><th>Calculated for
$C_{11}H_{12}O_2N_2S$.</th><th>Found.</th></tr>
<tr><td>N</td><td>11.86</td><td>11.77</td></tr>
</table>

This hydantoïn is very soluble in benzene and alcohol. It can be crystallized from a mixture of benzene and petroleum ether, or from dilute acetic acid. It agreed in every respect with the compound hitherto supposed to be the rhodanide.

NEW HAVEN, CONN., May, 1902.

II.—ON THE PREPARATION OF AROMATIC GUAN-IDINES.

By FREDERICK J. ALWAY AND CAREY E. VAIL.

While symmetrical triphenylguanidine is a well-known compound that has been prepared by a great variety of methods, and that can be obtained in pure condition without difficulty, the diphenyltolyl- and phenylditolylguanidines have been but little studied and their properties and reactions are even yet unknown, except in a very small number of cases. The influence of the position of a substituting group upon the course of the reactions in which the guanidines are formed appears to be very great. Marckwald[1] has shown that when an aromatic carbodiimide, $C(=N \cdot R)_2$, reacts with an aniline, $NH_2.R'$, compounds of three different classes may result, *viz.*:
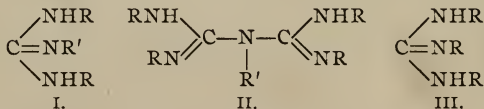
Diphenylcarbodiimide forms with aniline and with *p*-toluidine compounds I. and II., but with *o*-toluidine only a compound of type I. is formed. Di-*o*-tolylcarbodiimide with aniline forms I. and III. As these are the only cases in which the reactions have hitherto been studied, no generalization can safely be made as to the cause of the varying course of the reaction. Of the ten possible isomeric symmetrical tritolylguanidines only two, tri-*o*-tolyl- and tri-*p*-tolylguanidine,

[1] Ann. Chem. (Liebig), **286**, 343.

are known, and neither of these has been investigated to determine whether diguanides are formed at the same time. Of the six possible symmetrical phenylditolylguanidines only phenyl-di-*o*-tolylguanidine has been prepared. Of the three diphenyltolylguanidines only *p*-tolyl- and *o*-tolyl- compounds have been obtained. Diphenyl-*p*-tolylguanidine was obtained by Hofmann,[1] and later by Huhn,[2] and carefully investigated by Marckwald,[3] who also studied the formation and properties of diphenyl-*o*-tolylguanidine. Diphenyl-*m*-tolylguanidine has been prepared in this laboratory and will be described in a subsequent article. So, of the twenty possible symmetrical guanidines containing only phenyl or tolyl, or phenyl and tolyl groups, but four have hitherto been carefully studied, and in the formation of these four, as above pointed out, we have three different types of reactions.

While the preparation of triphenylguanidine presents no difficulties, that of the diphenyltolylguanidines and the phenylditolylguanidines, using analogous methods, has proved unsatisfactory on account of the difficulty of obtaining the pure base from the reaction-mixture. In 1886 Huhn[4] described two isomeric diphenyl-*p*-tolylguanidines, melting at 120° and 126° respectively. In the last edition of Beilstein these compounds are described as isomers. It was not easy to understand why these compounds should be accepted as isomers without the repetition of Huhn's work, when they, with the exception of a few amidines, were the only examples of isomers to which the different structural formulæ

$$X—C\diagup{NHR}\diagdown{NR'} \qquad \text{and} \qquad X—C\diagup{NR}\diagdown{NHR'}$$
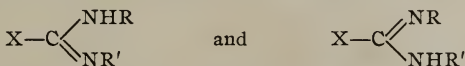
could be assigned, and at a time when Conrad Laar, who introduced the name and the idea of "tautomerism," could make the statement :[5] "Auf jenen (Tautomerie-) Begriff selbst brauche ich an dieser Stelle nicht wieder zurückzukom-

[1] Ber. d. chem. Ges., **2**, 459.
[2] *Ibid.*, **19**, 2412.
[3] *Loc. cit.*
[4] *Loc. cit.*
[5] Sitzungsberichte d. Niederrhein. Ges. f. Natur-u. Heilkunde, **5**, 6 (1893).

men, da er inzwischen zu allgemeiner Aufnahme gelangt ist.''

The repetition of Huhn's work and the investigation of other members of this class of bases showed that the alcoholic solution of the base, which results from the action of lead oxide upon a mixture of diphenylthiourea (1 mol.) and a toluidine (1 mol.), yielded an amorphous solid or a thick, oily liquid, from which only 2 to 5 per cent of the theoretical amount of guanidine could be obtained. Marckwald, who in 1895 showed that the compounds described by Huhn as isomers were really identical, and that a second base was mixed with the guanidine in the crude reaction-mixture in each case, has very kindly informed us in a private communication that he obtained a better yield from the carbodiimide and base than from the thiourea and base, and that he had no notes of the yield but believed the former method gave at least 20 per cent of the theoretical. By using the carbodiimide we obtained 40 per cent of the theoretical yield in some cases. Even when we used this method it was often found difficult to obtain the guanidine in pure condition. As the guanidines, when once obtained in pure form, crystallize from alcohol readily, we studied the salts of diphenyl-*p*-tolylguanidine with the idea of finding, if possible, one that could be readily obtained in the pure form and that, with alkalies, would give the pure base. It was found that the nitrate, which is but sparingly soluble in cold alcohol and which crystallizes well from this solvent, could easily be obtained pure, and that the base, liberated from this by an alkali, was practically pure and crystallized readily from alcohol. The same method seems capable of general application in the case of guanidines that contain two phenyl- and one tolyl- or one phenyl- and two tolyl- groups. The simplest method of preparing triphenylguanidine is that of Hofmann.[1] A mixture of aniline (1 mol.) and diphenylthiourea (1 mol.), in concentrated alcoholic solution, is treated with lead oxide or mercuric oxide. Various salts of these metals may be used instead of oxides. The mixture is kept boiling on a water-bath until desulphurization is complete and then filtered hot. The triphenylguani-

[1] Ber. d. chem. Ges., **2**, 458.

dine separates from the cooling filtrate in large, colorless crystals. The yield is almost quantitative.

Starting with carbon bisulphide, aniline, and a lead salt, the guanidine may be had in pure condition within an hour and a half. By using the methods of Hugershoff[1] or Braun,[2] diphenylthiourea may be obtained in pure condition within half an hour, instead of eight to twelve hours as by the older methods. A comparison of the different methods of preparing the thioureas, together with various modifications, is given in the experimental part of this article.

EXPERIMENTAL.

As the aromatic guanidines, with the exception of triphenylguanidine, have been obtained directly or indirectly only from thioureas, a convenient method of preparing the latter was important. Accordingly, we endeavored to determine which of the methods suggested is the most satisfactory. We found that lead hydroxide is a more satisfactory desulphurizing agent than any that has previously been described.

Preparation of Thioureas.

When a mixture of aniline, carbon bisulphide, and alcohol is heated on the water-bath for from three to fifteen hours, the mixture becomes almost solid from the formation of diphenylthiourea. The reaction takes place more quickly if solid potash is added, but the yield is thereby diminished. Hugershoff[3] showed that the reaction, in the above case, is due to the presence of sulphur dissolved in the carbon bisulphide and that, when sulphur was added before heating, the reaction was complete at the end of an hour. Later, Braun[4] showed that by shaking a mixture of aniline (2 mols.) and carbon bisulphide (1 mol.) with an aqueous solution of hydrogen peroxide (1 mol.) the same thiourea was formed. We found that by using only carbon bisulphide (5 parts), aniline (5 parts), and sulphur (1 part), the reaction was practically complete at the end of fifteen minutes. While by Braun's

[1] Ber. d. chem. Ges., **32**, 2245.
[2] *Ibid.*, **33**, 2727.
[3] *Loc. cit.*
[4] *Loc. cit.*

method evolution of hydrogen sulphide is avoided and the reaction takes place as quickly as when the last described method is used, the crude reaction-product, which contains about 10 per cent of sulphur, must be freed from water before it is treated with carbon bisulphide. In both cases the sulphur may be extracted by carbon bisulphide, the diphenylthiourea remaining in pure crystalline condition. Instead of removing the sulphur in this way the unchanged carbon bisulphide may be driven off by warming the reaction-mixture on the water-bath, and the thiourea then recrystallized from alcohol. The first method of purification was found preferable, requiring much less time and giving a better yield of pure thiourea.

Desulphurizing Agents.

The chief of these whose action has hitherto been described are mercuric oxide and lead oxide. The salts of lead and mercury were not found satisfactory, the product consisting of a mixture of base and salt, and the reaction proceeding slowly. The best reagent seems to be lead hydroxide, freshly prepared by treating lead nitrate solution in the cold with ammonium hydroxide and washing the precipitate with water until the diphenylamine test shows the absence of nitrate. The hydroxide is filtered out under suction and mixed with alcohol to form a thin paste. If the reaction-mixture is allowed to become warm or if the hydroxide is preserved for any considerable length of time, the fine precipitate, at first obtained, becomes coarse and granular. When this coarse form is used a great excess of the lead hydroxide is required to desulphurize the thiourea. The small amount of lead compound required, the rapidity of the reaction, and the ease with which its course may be followed, are the chief arguments in favor of its use. On the other hand, it must be freshly prepared and thoroughly washed. If the last precaution is omitted, the hydroxide will contain some ammonium nitrate, which causes the formation of more or less guanidine nitrate.

Preparation of Guanidines.

The thiourea and amine, in equimolecular amounts, are

dissolved in ordinary alcohol and the mixture heated to boiling on the water-bath. Then an excess of lead hydroxide, prepared as above described, is added to the mixture and the heating continued until a portion of the filtered alcoholic solution, when boiled with lead hydroxide, produces no blackening. The rate of desulphurization depends upon the nature of the thiourea. Witt has shown that it is probable that the carbodiimide is first formed and that this then combines with the base.

When diphenylthiourea was used the reaction was complete at the end of ten minutes, but when phenyl-*p*-tolylthiourea and di-*p*-tolylthiourea were employed, half an hour and two hours, respectively, were required. The hot reaction-mixture is filtered under suction and the black residue, consisting chiefly of lead sulphide, is extracted with small quantities of boiling alcohol until the last portion, when filtered and treated with an excess of water, remains clear. In the preparation of diphenyl-*p*-tolylguanidine the eighth and ninth portions of alcohol gave a white deposit on cooling. This, when recrystallized, gave colorless needles melting at 128° to 129°, the melting-point of the guanidine. The diguanide, which forms in small quantities and which, being only slightly soluble in aqueous alcohol, remains mixed with the lead sulphide, is evidently decomposed by prolonged heating in alcoholic solution to form the corresponding guanidine. The clear solution contains a large amount of the guanidines, but, on standing, deposits either no crystals at all or at most only from 2 to 5 per cent of the theoretical amount. By complete evaporation of the alcohol a gummy mass is obtained. When the above solution, kept cool by ice-water, is treated with a slight excess of concentrated nitric acid, it becomes red and crystals soon begin to separate out. At the end of two hours the separation is usually complete. The crystals are filtered out, washed with a little cold alcohol, and dried. Sometimes they are colored pink, in which case they are dissolved in alcohol and the solution boiled with animal charcoal. The nitrate so obtained is recrystallized until the melting-point remains constant and then dissolved in warm alcohol. After adding a few

drops of phenolphthalein the solution is treated with dilute potash until it shows a faint alkaline reaction. In the preparation of phenyldi-*o*-tolylguanidine a small amount of tri-*o*-tolylguanidine is formed at the same time. It was found that to obtain the latter compound it was best to change the mixture of nitrates, after it had been once recrystallized from alcohol, into the corresponding guanidines which were then separated by recrystallization.

In the preparation of diphenyl-*p*-tolylguanidine, the formation of no other guanidine was detected. When the nitrate in this case was recrystallized from alcohol until the melting-point remained constant, the pure base could be obtained by treating the warm solution of the nitrate in aqueous alcohol with dilute potash, and then allowing it to cool slowly.

In all cases investigated, with the exception of tri-*m*-tolylguanidine, the yield of nitrate or of the mixture of nitrates was from 75 to 90 per cent of the theoretical. The nitrate of tri-*m*-tolylguanidine was not obtained by the general method.

As the whole subject of the action of aromatic amines upon carbodiimides as well as upon thioureas is under investigation in this laboratory, we will describe only the nitrate of diphenyl-*p*-tolylguanidine of which the corresponding base and hydrochloride have been previously described by Marckwald.[1]

Diphenyl-*p*-tolylguanidine nitrate was obtained in equally good yield from diphenylthiourea with *p*-toluidine, and from phenyl-*p*-tolylthiourea with aniline. It forms small, colorless plates, melting at 196° to 197°, readily soluble in hot alcohol, slightly soluble in cold alcohol and hot water, and very slightly soluble in cold water.

	Calculated for $C_{20}H_{19}N_3 \cdot HNO_3$.	Found.
HNO_3	17.30	17.68

The nitrates of the following bases have been obtained by the general method given above: diphenyl-*m*-tolyl-, phenyldi-*p*-tolyl-, *o*-tolyldi-*p*-tolyl-, *m*-tolyldi-*p*-tolyl-, di-*o*-tolyl-*p*-tolyl-, di-*o*-tolyl-*m*-tolyl-, and phenyl-*o*-tolyl-*p*-tolylguanidine.

[1] *Loc. cit.*

AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Case School of Applied Science.

XLI.—THE COMPOSITION OF PETROLEUM.

ON THE HYDROCARBONS IN PENNSYLVANIA PETROLEUM WITH BOILING-POINTS ABOVE 216°.

By Charles F. Mabery.

In a former paper[1] the principal hydrocarbons in Pennsylvania, Ohio, and Canadian petroleum with boiling-points below 216°, were shown to have the composition represented by the general formula C_nH_{2n+2}. Concerning the constituents with higher boiling-points very little is known. Pelouze and Cahours[2] collected distillates to which they gave the following formulas:

216°–218°	236°–240°	255°–260°	280°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

From paraffin the following hydrocarbons have been separated (Beilstein's Handbook):

212°–215°	230°–235°	252°–255°	273°–275°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

[1] Proc. Am. Acad., **32**, 121.
[2] Ann. chim. phys., [4], **1**, 5 (1864).

So far as I am aware these are the only allusions to the composition of Pennsylvania petroleum in these portions. It appears that the distillations were made under ordinary atmospheric pressure in presence of air, with no attempts to avoid decomposition under these conditions.

Then, furthermore, as I have suggested in a former paper, the high specific gravity of the distillates separated by Pelouze and Cahours indicate that their distillates were obtained from Canadian petroleum. It does not appear that any attempts have been made to ascertain the molecular weights of the individual hydrocarbons. Indeed, this has been possible only within recent years, since the freezing- and boiling-point methods for the determination of molecular weights have been known. Then it is not possible to determine the vapor densities of these hydrocarbons, because, as I have recently ascertained, even *in vacuo* small quantities of the hydrocarbons such as are used in vapor density determinations undergo serious decomposition ; and this occurs even in oils that have been distilled many times over in bulk *in vacuo*. In the earlier work it was evidently assumed that a few distillations under atmospheric pressure were sufficient to collect the individual hydrocarbons within the limits of their boiling-points, sufficient at least to afford reliable data as to their composition. A glance at the small differences in percentage composition is sufficient to show that it is not possible by analysis alone of products even well purified to distinguish between homologous members of a series, although such analysis may define the series.

But the chief difficulty is to obtain each hydrocarbon uncontaminated by any admixture of its homologues or by products of decomposition. This is well illustrated by the experience of Markownikoff in separating the hydrocarbons in the Russian oil, who found it impossible to collect distillates closer than limits of 5° on account of decomposition. That the same is true, perhaps in a less degree, in distillates from Pennsylvania oil is evident whenever distillation is made of the higher portions under atmospheric pressure. The rank odor is evidence of cracking. Yet the constituents with higher boiling-points are under the influence of vapor tension as much as the

constituents with lower boiling-points, and consequently require as prolonged distillation for complete or approximately complete separation. |In my experience it is only possible to obtain even an approximate separation by exclusion of air and depression of boiling-points.|

| In this manner the higher hydrocarbons may be distilled any number of times with no appreciable decomposition. The only limit is the patience of the operator. But the stability of these hydrocarbons is evidently dependent on the influence of mass. Since, as mentioned above, while distillation of any considerable quantity of the oil may be carried on indefinitely, a limited quantity cannot be volatilized even *in vacuo* without decomposition. Many attempts to determine the vapor density of the hydrocarbons in Pennsylvania and California petroleum by volatilization *in vacuo*, according to the method of Lunge and Neuberg, have failed on account of cracking, even so far as the separation of sooty carbon from the members with high boiling-points. |

In September, 1896, I set out to ascertain the composition of the principal hydrocarbons in Pennsylvania petroleum with boiling-points above 216° so far as they can be separated by distillation on a laboratory scale. Through the courtesy of the Standard Oil Company, I procured a barrel of crude oil from Oil City, and this material has been used to separate the hydrocarbons that will be described in this paper. That this oil was an approximately average specimen of Pennsylvania petroleum, appears from its properties. |A determination of the specific gravity of the crude oil at 20° gave 0.8095.| A combustion of the oil dried over sodium gave the following percentages of carbon and hydrogen: |Carbon, 85.80; hydrogen, 14.04.| Eight hundred grams distilled in the ordinary way in the following proportions:

50°–150°	150°–200°	200°–250°	250°–300°	+300°
166	88	83	100	337

Fifty-six kilograms of the crude oil were distilled in quantities of 10 liters each in a porcelain still, collecting under atmospheric pressure to 200°, and within limits of 10° under a

vacuum of 50 mm. to 300°, then within limits of 5°, and finally within limits of 2°. After eight distillations the following proportions collected :

124°–126° 136°–138° 156°–158° 174°–176° 188°–199°
Grams, 125   145   240   205   240

199°–201° 210°–212° 226°–228° 242°–244°
225   335   150   130

Since the weights of these fractions represent all that came from the original crude oil, it is possible to gain a very general idea of the proportion of the hydrocarbons which are contained in the crude oil. But such estimation must be only approximate from the fact that any distillation, however thorough, gives only an approximate separation, and a considerable portion of any hydrocarbon must be contained in the intermediate distillates.

The percentages of the weights are as follows :

$C_{13}H_{28}$ $C_{14}H_{30}$ $C_{15}H_{32}$ $C_{16}H_{34}$ $C_{17}H_{36}$
124°–126° 136°–138° 156°–158° 174°–176° 188°–199°
0.22   0.26   0.43   0.37   0.43 per cent

$C_{18}H_{38}$ $C_{19}H_{40}$ $C_{20}H_{42}$ $C_{21}H_{44}$
199°–201°   210°–212°   230°–232°   242°–244°
0.40   0.60   0.27   0.23 per cent

In the intervals between these fractions the weights were much smaller.

After the eighth distillation each fraction was agitated at first with common concentrated sulphuric acid until the acid was not much colored, and then several times with fuming sulphuric acid. That the distillates consist almost entirely of the principal hydrocarbon is shown by the slight change in specific gravity by the acid treatment :

156°–158°   174°–176°   182°–184°
0.805   0.8064   0.8100   Original distillate.
0.7992   0.8031   0.8093   After treatment with acid.

There was some loss in weight of the fraction by the acid treatment, but it was doubtless due, for the most part, to solution of the principal hydrocarbons in the acid. The weights of the fractions before and after treatment were as follows :

156°–158°	174°–176°	182°–186°
240	215	205
195	190	155

This solvent action has been observed in other oils with high boiling-points in continuous treatment with fuming sulphuric acid, which caused a gradual loss without changing materially the specific gravity. | After the purification with the acid, distillation was continued through a Hempel column filled with glass beads or broken glass, under 50 mm. within limits of 1°, until the hydrocarbons collected in considerable quantities. | After the thirtieth distillation the hydrocarbons came together within the following limits :

124°–126° 142°–143° 158°–159° 173°–174° 189°–190° 198°–199°

Even after nearly continuous distillation of sixteen months, these products showed very little indication of decomposition. Leaks in the apparatus immediately cause decomposition, as shown by a disagreeable odor, and the appearance of the distillates. So long as air is excluded from the hot vapors there is no danger of decomposition. But as we found, in attempting to ascertain the boiling-points under atmospheric pressure, a single distillation in air causes a very rank odor of decomposition.[1]

In determining the boiling-points of these hydrocarbons under atmospheric pressure, 70 grams of the fraction 124°–126° distilled as follows, under 760 mm. and with the mercury column all within the vapor :

	224°–225°	225°–226°	226°–227°	227°–228°	228°–229°
Grams,	4	28	26	3	3
			Colored residue, 6		

The portions between 225° and 227° collected almost entirely between 225°.5 and 226°.5.

The fraction 142°–143° nearly all distilled at 237°–238° atmospheric pressure, the fraction 158°–159° at 256° to 257°, the

[1] The difference in stability of the constituents of different petroleums is shown by their behavior when air comes in contact with the hot vapors. In accidents that have occurred during distillation, letting in air on the hot vapors, in the case of Pennsylvania petroleum the still becomes filled with dark vapors, but in a distillation of Russian petroleum, air accidentally admitted caused such a violent explosion that the thermometer was hurled across the room and broken against the wall.

raction 173°–174° at 274° to 275°, the fraction 188°–189° at 288° to 289°, and the fraction 198°–199° at 300° to 301° The hydrocarbon dodecane, $C_{12}H_{26}$, was identified in the fraction 214°–216°.[1]

Tridecane, $C_{13}H_{28}$.—The next homologue, tridecane, was sought for in the series of distillates that collected between 215° and 235°. After carrying these fractions eight times through a Hempel bead column a larger portion, 200 grams, collected at 221° to 222°. This portion was distilled twenty-four times, when 70 grams collected, as shown above. The specific gravity of the distillate before further treatment was 0.7866, and after thorough agitation with fuming sulphuric acid, 0.7834. A combustion gave the following values for carbon and hydrogen :

0.1506 gram of the oil gave 0.4690 gram CO_2 and 0.2028 gram H_2O.

	Calculated for $C_{13}H_{28}$.	Found.
C	84.78	84.94
H	15.22	14.96

The molecular weight of this oil, as determined by the Beckmann method at the freezing-point of benzene, in the hands of different workers, corresponds to that of $C_{13}H_{28}$.

I. 1.1209 grams oil and 36.3043 grams benzene gave a depression of 0°.82.

II. 1.2502 grams oil and 33.3631 grams benzene gave a depression of 1°.015.

III. 1.496 grams oil and 32.9131 grams benzene gave a depression of 1°.205.

Calculated for $C_{13}H_{28}$.	I.	Found. II.	III.
184	184.5	181	184.9

In still further confirmation of the formula of tridecane, the index of refraction was determined and its molecular refraction calculated. The index was found to be 1.4354 at 20°, and the molecular refraction as follows :

Calculated for $C_{13}H_{28}$.	Found.
61.94	61.44

[1] Proc. Am. Acad., **32**, 138.

Monochlortridecane, $C_{13}H_{27}Cl$.—In the preparation of the chlorine derivative of tridecane, chlorine was allowed to act on the hydrocarbon in screened sunlight, over water. With care to avoid an excess of chlorine, the product consisted for the most part of the monochloride. It was fractioned several times *in vacuo* under 12 mm. until considerable of the oil collected at 135° to 140°. This fraction gave as its specific gravity, at 20°, 0.8973. A determination of chlorine gave the percentage required for the monochloride:

0.1920 gram oil gave 0.1273 gram AgCl.

	Calculated for $C_{13}H_{27}Cl$.	Found.
Cl	16.23	16.39

The molecular weight as determined at the freezing-point of benzene corresponded to the same formula:

0.4585 gram oil and 18.35 grams benzene gave a depression of 0°.568.

Calculated for $C_{13}H_{27}Cl$.	Found.
218.5	216

A determination of the index of refraction confirmed the same formula; the index as determined was 1.451, corresponding to the molecular refraction:

Calculated for $C_{13}H_{27}Cl$.	Found.
65.71	66.67

Tetradecane, $C_{14}H_{30}$.—The fraction 142°–143°, collected after tl twenty-fourth distillation, had the specific gravity 0.7848, after drying over sodium. After agitating with concentrated sulphuric acid, washing, and drying over sodium, it gave 0.7847. After treatment with fuming sulphuric acid it gave 0.7814. This determination, like the others, was made at 20°.

A determination of the molecular weight of this fraction, purified with fuming sulphuric acid, gave the following result:

I. 1.1049 grams oil and 36.8505 grams benzene gave a depression of 0°.735.

II. 1.052 grams oil and 35.970 grams benzene gave a depression of 0°.718.

	Calculated for $C_{14}H_{30}$.	Found.	
		I.	II.
	198	199.9	199.5

A combustion gave the following percentages of carbon and hydrogen :

0.1502 gram oil gave 0.4698 gram CO_2 and 0.2024 gram H_2O.

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	85.02
H	15.16	14.96

This specimen was purified with common concentrated acid; another portion purified with fuming sulphuric acid gave slightly different proportions :

0.1458 gram oil gave 0.4532 gram CO_2 and 0.1970 gram H_2O.

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	84.76
H	15.16	15.02

The boiling-point of this fraction under 760 mm. was 236° to 238°. On account of decomposition when the oil is distilled in air, it is difficult to determine the boiling-point with great precision.

A determination of the index of refraction of this hydrocarbon gave 1.4360, which corresponds to the following molecular refraction :

	Calculated for $C_{14}H_{30}$.	Found.
	66.54	66.36

Monochlortetradecane, $C_{14}H_{29}Cl$.—Since only small quantities of the purified hydrocarbons were available for the study of the chlorides, great care was necessary to avoid too high chlorination. Most of the hydrocarbons gave only sufficient of the chlorine derivative to verify its formula by the percentage of chlorine. The chlorine product obtained from tetradecane was fractioned *in vacuo* until it collected in larger quantities at 150°–153° under 20 mm. A determination of chlorine gave the following result :

0.1966 gram oil gave 0.1245 gram AgCl.

	Calculated for $C_{14}H_{29}Cl$.	Found.
Cl	15.25	15.65

Its specific gravity at 20° was found to be 0.9185. The quantity of product was not enough for other determinations. Another portion of the chlorine product, collected at 175° to 180°, 17 mm., gave as its specific gravity, at 20°, 1.032. A determination of chlorine gave the value required for the dichloride:

0.1937 gram oil gave 0.2125 gram AgCl.

	Calculated for $C_{14}H_{28}Cl_2$.	Found.
Cl	26.55	27.12

A determination of molecular weight at the freezing-point of benzene showed it to be the dichloride:

1.3407 grams oil and 19.81 grams benzene gave a depression of 1°.255.

Calculated for $C_{14}H_{28}Cl_2$.	Found.
267	264.3

Pentadecane, $C_{15}H_{32}$.—The specific gravity of the fraction 158°–159° (50 mm.), dried over sodium, was found to be 0.8054 at 20°. After treatment with concentrated sulphuric acid it gave 0.7939, and after thorough treatment with fuming sulphuric acid it gave 0.7896.

The molecular weight was determined by the Beckmann method:

I. 1.050 grams oil and 35.9775 grams benzene gave a depression of 0°.675.

II. 1.3946 grams oil and 23.2679 grams benzene gave a depression of 1°.37.

Calculated for $C_{15}H_{32}$.	Found.	
	I.	II.
212	211	212

Combustion I. was made of the unpurified distillate dried over sodium, and combustion II. of the oil after treatment with fuming sulphuric acid:

I. 0.1440 gram oil gave 0.4500 gram CO_2 and 0.1919 gram H_2O.

II. 0.1608 gram purified oil gave 0.5002 gram CO_2 and 0.2198 gram H_2O.

	Calculated for $C_{15}H_{32}$.	Found.	
		I.	II.
C	84.92	85.21	84.87
H	15.08	14.80	15.20

In determining the boiling-point of pentadecane, under atmospheric pressure, it distilled almost completely at 256° to 257°.

A determination of the index of refraction gave 1.4413, from which the molecular refraction was calculated :

Calculated for $C_{15}H_{32}$.	Found.
71.15	70.49

Dichlorpentadecane, $C_{15}H_{30}Cl_2$.—With the small quantity of the hydrocarbon at hand, we did not succeed in limiting the action of chlorine to the formation of the monochloride. Fractioned *in vacuo* under 13 mm. the chlorinated product collected for the most part at 175° to 180°. This product gave as its specific gravity, at 20°, 1.0045. A Carius determination of chlorine gave the following percentage :

0.1411 gram oil gave 0.1462 gram AgCl.

	Calculated for $C_{15}H_{30}Cl_2$.	Found.
Cl	25.28	25.63

The molecular formula was established by a determination of its molecular weight :

1.4308 grams oil and 18.53 grams benzene gave a depression of 1.336.

Calculated for $C_{15}H_{30}Cl_2$.	Found.
281	283.2

Hexadecane, $C_{16}H_{34}$.—The fraction that collected at 174° to 175°, 50 mm., after the thirtieth distillation gave as its specific gravity, at 20°, 0.8000. After treatment with concentrated sulphuric acid it gave 0.7964, and after treatment with fuming sulphuric acid, 0.7911. It distilled almost completely at 275° to 276° under 760 mm. barometric pressure. In determining the molecular weight of this fraction at the freezing-point of benzene, it gave the formula $C_{16}H_{34}$:

I. 1.1507 grams oil and 35.27 grams benzene gave a depression of 0°.71.

II. 1.1833 grams oil and 35.63 grams benzene gave a depression of 0°.715.

Calculated for $C_{16}H_{34}$.		Found.	
		I.	II.
226		225.2	227.6

Determinations of carbon and hydrogen were made in the unpurified distillate (I.), in a portion purified with concentrated sulphuric acid (II.), and in a third portion purified with fuming sulphuric acid (III.), with the following results :

I. 0.1477 gram oil gave 0.4600 gram CO_2 and 0.1973 gram H_2O.

II. 0.1454 gram oil gave 0.4522 gram CO_2 and 0.1986 gram H_2O.

III. 0.1454 gram oil gave 0.4516 gram CO_2 and 0.1971 gram H_2O.

	Calculated for $C_{16}H_{34}$.	I.	Found. II.	III.
C	84.96	84.94	84.80	84.60
H	15.04	14.84	15.18	15.06

The index of this hydrocarbon was found to be 1.4413, from which the molecular refraction was calculated :

Calculated for $C_{16}H_{34}$.	Found.
75.750	75.555

Dichlorhexadecane, $C_{16}H_{33}Cl_2$.—The chlorine product obtained from hexadecane collected for the larger part at 205° to 210°, under 16 mm. Its specific gravity was 1.0314 at 20°. A determination of chlorine gave a value required for the dichloride :

0.1477 gram oil gave 0.1525 gram AgCl.

	Calculated for $C_{16}H_{32}Cl_2$.	Found.
Cl	24.61	24.44

This formula was also confirmed by its molecular weight :

0.5019 gram oil and 18.21 grams benzene gave a depression of 0°.457.

Calculated for $C_{16}H_{22}Cl_2$.	Found.
295	295

A portion of the original distillate 174°–175° was cooled to —10°, which caused the separation of a crystalline mass. It was filtered cold, but the solid remaining formed but a small part of the original oil.

The specific gravity of the filtered oil, 0.8005, was slightly higher than that of the unfiltered distillate. The quantity of the solid was not sufficient for analysis or further examination. No further examination was made of the filtered oil, for it was evident that the small amount of solid hydrocarbon could not change the composition nor other constants, especially since, as shown above, the original distillate has the composition of the series C_nH_{2n+2}.

Heptadecane, $C_{17}H_{36}$.—The fraction which collected at 188° to 190° after the forty-second distillation gave as its specific gravity, at 20°, after drying over sodium, 0.8017. After agitation with sulphuric acid it gave 0.8019, and after purification with fuming sulphuric acid, 0.8000. Under 760 mm. pressure this oil distilled almost entirely at 288° to 289°, with very little residue above 289°. The small residue was badly colored from decomposition. Evidently it would not be possible to distil this oil continuously under atmospheric pressure in presence of air without serious decomposition.

The formula of this distillate was established by two determinations of its molecular weight and by analysis.

I. 1.4294 grams oil and 25.7086 grams benzene gave a depression of 1°.17.

II. 1.4382 grams oil and 25.6785 grams benzene gave a depression of 1°.18.

Calculated for $C_{17}H_{36}$.	Found.	
	I.	II.
240	241.2	240.9

Analysis I. was made of the unpurified oil dried over sodium, and analysis II. after purification with fuming sulphuric acid.

I. 0.1534 gram oil gave 0.4778 gram CO_2 and 0.2044 gram H_2O.

II. 0.1491 gram oil gave 0.4641 gram CO_2 and 0.2014 gram H_2O.

	Calculated for $C_{17}H_{36}$.	I.	II.
C	84.96	84.94	84.87
H	15.04	14.80	15.01

Monochlorheptadecane, $C_{17}H_{35}Cl$.—The chlorine product from heptadecane collected in considerable quantity at 175° to 177° (15 mm.). Its specific gravity, at 20°, was found to be 0.8962. The percentage of chlorine corresponded to the monochloride:

0.1510 gram oil gave 0.0807 gram AgCl.

	Calculated for $C_{17}H_{35}Cl$.	Found.
Cl	12.92	13.21

On cooling a portion of the distillate 188°–189° to —10° it formed a pasty mass from which a small amount of a crystalline solid was obtained by filtration. The solid, after crystallization from ether and alcohol, melted at approximately 10°. The amount of solid was not sufficient for purification or examination. The filtered oil gave as its specific gravity, at 20°, 0.8035, slightly higher than that of the distillate before filtration. Since the original distillate had the composition of the series C_nH_{2n+2}, it did not seem worth while to make any further examination of the filtered oil.

Octodecane, $C_{18}H_{38}$.—After the twenty-sixth distillation larger quantities of distillates collected between 198° and 204°, mostly at 199° to 200° (50 mm.). The fraction 199°–200° distilled for the most part, although with considerable colored residue and bad odor, at 300° to 301°, under 760 mm. After drying over sodium its specific gravity was 0.8054, after agitation with sulphuric acid 0.8035, and after purification with fuming sulphuric acid 0.8017, at 20°.

Its molecular weight was ascertained by the Beckmann method at the freezing-point.

I. 0.9963 gram oil and 36.4129 grams benzene gave a depression of 0°.53.

II. 0.9926 gram oil and 23.2544 grams benzene gave a depression of 0°.84.

Calculated for $C_{18}H_{38}$.		Found.	
		I.	II.
254		252.7	254.2

Combustion I. was made of the unpurified distillate dried over sodium ; combustion II., of the oil after purification with concentrated sulphuric acid; and combustion III., after treatment with fuming sulphuric acid.

I. 0.1423 gram oil gave 0.4435 gram CO_2 and 0.1915 gram H_2O.

II. 0.1513 gram oil gave 0.4702 gram CO_2 and 0.2054 gram H_2O.

III. 0.1524 gram oil gave 0.4727 gram CO_2 and 0.2064 gram H_2O.

	Calculated for $C_{18}H_{38}$.	I.	Found. II.	III.
C	85.06	85.02	84.76	84.59
H	14.94	14.96	15.09	15.05

It is evident from the slight change in specific gravity after purification, and the percentages of carbon and hydrogen, that the original distillate consisted to a large extent of octodecane.

Monochloroctodecane, $C_{18}H_{37}Cl$.—The product obtained by the action of chlorine on octodecane collected in greater part at 185° to 190°, under 15 mm., and this fraction gave as its specific gravity, at 20°, 0.9041. The percentage of chlorine corresponded to the monochloride :

0.1482 gram oil gave 0.0782 gram AgCl.

	Calculated for $C_{18}H_{37}Cl$.	Found.
Cl	12.35	13.05

The results given above were obtained with the hydrocarbon that was liquid at ordinary temperatures. When it was found that crystals separated from this distillate at 3°, and that it became pasty at 0°, it was cooled to —10°, when it became so thick that it filtered only slowly. The solid, after filtering, was melted and again cooled and filtered, after which it was perfectly white. It was then crystallized from ether and alcohol, after which it melted at 20°. It was estimated that 20 per cent of the original oil separated as the solid hy-

drocarbon on cooling. It was difficult to separate the solid completely on account of the great solvent action of the oil.

The filtered and pressed solid melted at 20°, and after crystallization from ether and alcohol and from gasoline, the melting-point could not be raised. Krafft[1] gave 28° as the melting-point of octodecane which he obtained from stearic acid, but his octodecane boiled at 214°.5 under 50 mm. pressure. The specific gravity of the solid hydrocarbon was 0.7830 at $\frac{20°}{20°}$, and 0.7816 at $\frac{20°}{40°}$. Krafft gave 0.7768 as the specific gravity of $C_{18}H_{38}$ at 28°. A determination of the molecular weight of the purified hydrocarbon confirmed its formula :

1.1003 grams oil and 19.65 grams benzene gave a depression of 0°.941.

Calculated for $C_{18}H_{37}Cl$.	Found.
288.5	291.5

This molecular weight, showing that the hydrocarbon boiling at 300° is octodecane, does not agree with Krafft's conclusion as to the formula of the hydrocarbon obtained from stearic acid. In heating stearic acid with hydriodic acid Krafft assumed that all the oxygen is removed, leaving intact the carbon of the carboxyl, with the formation of octodecane. But when this work was done the only means of verifying the formula was by analysis, which was sufficient to determine the series, but not the individual members of the series. While the results of Krafft's combustions gave almost exact values for the formula $C_{18}H_{38}$, the size of the molecule could not be determined. Krafft looked upon the hydrocarbon boiling at 303° as having the formula $C_{17}H_{36}$.

The specific gravity of the oil, after cooling and filtration, was somewhat higher than before, 0.8110 at 20°, and higher than the specific gravity of the filtered solid octodecane, 0.7830. The molecular weight of the filtered oil was the same as before filtration.

0.9904 gram substance and 16.10 grams benzene gave a depression of 1°.184.

Calculated for $C_{18}H_{38}$.	Found.
254	254.6

[1] Ber. d. chem. Ges., **15**, 1703 (1882).

A combustion of the liquid hydrocarbon showed some change in the proportion of carbon and hydrogen :

0.1483 gram substance gave 0.4636 gram CO_2 and 0.1954 gram H_2O.

	Calculated for		Found.
	$C_{18}H_{36}$.	$C_{18}H_{38}$.	
C	85.70	85.06	85.25
H	14.30	14.94	14.64

While there is a narrow difference in calculated percentages between the two formulæ, the percentages found, together with the higher specific gravity, indicate that the filtered oil was a mixture of the two series C_nH_{2n} and H_nC_{2n+2}.

A determination of the index of refraction, which was found to be 1.4435, and the molecular refraction correspond more nearly to the formula $C_{18}H_{36}$:

Calculated for		Found.
$C_{18}H_{36}$.	$C_{18}H_{38}$.	
82.90	84.96	82.60

A combustion of the solid hydrocarbon gave proportions required for the series C_nH_{2n+2} :

0.1564 gram substance gave 0.4883 gram CO_2 and 0.2083 gram H_2O.

	Calculated for	Found.
	$C_{18}H_{38}$.	
C	85.06	85.15
H	14.94	14.80

The position in the series was shown by its molecular weight :

I. 1.9475 grams of the solid and 25.21 grams benzene gave a rise of $0°.7734$.

II. 1.9475 grams of the solid and 25.28 grams benzene gave a rise of $0°.7830$.

Calculated for	Found.	
$C_{18}H_{38}$.	I.	II.
254	256	253.2

The formula of octodecane was further confirmed by its index of refraction. The index was found to be, at 20°, 1.440, which corresponds to the molecular refraction :

Calculated for	Found.
$C_{18}H_{38}$.	
84.96	84.53

Nonodecane, $C_{19}H_{40}$.—In the eighth distillation, under 50 mm., 335 grams collected at 210° to 212° with much smaller weights on either side. After continuing the distillation twenty-seven times, a portion of the fraction 210°–212° was purified with fuming sulphuric acid; before this treatment the oil gave as its specific gravity, at 20°, 0.8274, and afterward, 0.8122. In determining its molecular weight by the freezing-point method the following values were obtained:

I. 1.1039 grams oil and 39.7462 grams benzene gave a depression of 0°.575.

II. 1.1418 grams oil and 36.2175 grams benzene gave a depression of 0°.505.

Calculated for $C_{19}H_{40}$.	Found.	
	I.	II.
268	269.5	268

Determinations of carbon and hydrogen gave values for the series C_nH_{2n+2}:

I. 0.1530 gram oil gave 0.4771 gram CO_2 and 0.1994 gram H_2O.

II. 0.1591 gram oil gave 0.4976 gram CO_2 and 0.2132 gram H_2O.

	Calculated for		Found.	
	$C_{19}H_{38}$.	$C_{19}H_{40}$.	I.	II.
C	85.70	85.08	85.04	85.29
H	14.30	14.92	14.48	14.89

Analysis I. was made of the oil before purification, and analysis II. afterward.

A determination of the index of refraction gave 1.4522, which corresponds to the following molecular refraction:

Calculated for $C_{19}H_{40}$.	Found.
89.55	88.68

The results on the composition of the distillate 210°–212° were obtained on the purified distillate without cooling to separate the solid hydrocarbon. On cooling a portion of this distillate to —10°, filtering cold and pressing the solid, 5 grams of the solid hydrocarbon and 30 grams of the liquid hydrocarbon were obtained; the solid hydrocarbon, therefore, formed a small part of the original distillate. The specific gravity of

the filtered oil was 0.8208 at 20°.   The specific gravity of the distillate before cooling, as shown above, was 0.8122 at 20°.

After crystallization from ether and alcohol, the specific gravity of the solid hydrocarbon was 0.7725 at $\frac{30°}{8.0°}$ and 0.7781 at $\frac{30°}{4.0°}$.

A determination of its molecular weight gave a value required for the hydrocarbon $C_{19}H_{40}$.

1.4011 grams of the solid and 26.66 grams benzene gave a rise of 0°.496.

Calculated for $C_{19}H_{40}$.	Found.
268	271.6

The melting-point of the solid was found to be 33° to 34°, corresponding to the melting-point, 32°, that Krafft found for the solid hydrocarbon distilling at 226°.5, 50 mm.

A combustion of the oil filtered from the solid hydrocarbon gave percentages of carbon and hydrogen required for $C_{19}H_{38}$:

0.1495 gram oil gave 0.4715 gram CO_2 and 0.1928 gram H_2O.

Calculated for $C_{19}H_{38}$.	Found.
85.70	86.00
14.30	14.33

A determination of the molecular weight confirmed the formula.

2.5445 grams oil and 24.63 grams benzene gave a rise of 0°.994.

Calculated for $C_{19}H_{38}$.	Found.
266	267

The formula was further verified by its index of refraction.

It gave the index 1.4515, corresponding to the molecular refraction :

Calculated for $C_{19}H_{38}$.	Found.
87.46	87.51

With the distillate 212°–214°, 50 mm., the limit is reached of the solid hydrocarbons whose molecular weight can be determined by the freezing-point method on account of the crys-

tallization of the hydrocarbon before the benzene freezes. The molecular weights of solid higher members were determined by the boiling-point method.

The results described in this paper defining the physical properties and formulas of the hydrocarbons separated from Pennsylvania petroleum differ in several essential particulars both from the hydrocarbons obtained by Krafft by decomposition of the monobasic acids with high molecular weights, and those formerly reported as among the constituents of Pennsylvania oil. It has been shown that the hydrocarbon which boils at 196° is undecane, $C_{11}H_{24}$, and not dodecane as found by Pelouze and Cahours. Likewise, the hydrocarbon which boils at 216° proved to be dodecane and not tridecane. Since there was no method for ascertaining the molecular weights of these bodies at the time when they were separated by Pelouze and Cahours, and elementary analysis could only determine the series, it was only by analogy that the homologous members of the series could be guessed at. Since 182° was accepted as the boiling-point of undecane, naturally dodecane and tridecane should fall into the fractions which boil at 196° and 216°.

The boiling-point of tridecane has been variously stated at 219°, 216°, and 212° to 215°. But neither of these temperatures can be accepted as the boiling-points of tridecane since its molecular weight is found to be that of the hydrocarbon boiling at 225° to 226°.

The hydrocarbon tetradecane boils at 236° to 238°, the same boiling-point as was assigned to the tridecane separated by Pelouze and Cahours, but the specific gravity of tetradecane, 0.7812 at 20°, is essentially lower than that found by Pelouze and Cahours, 0.809.

Pentadecane, boiling-point 156° to 157°, is nearly the same in boiling-point as the hydrocarbon separated by Pelouze and Cahours, boiling-point 260°, although its specific gravity, 0.7896 at 20°, is much lower than they found, —0.825 at 19°.

The boiling-point of hexadecane is not very different from that given by Pelouze and Cahours, but its specific gravity is considerably lower. It does not differ materially in boiling-

point from hexadecane, which Krafft obtained by heating palmitic acid, nor from that of hexadecane, boiling-point 278°, obtained by Zincke from normal octyl iodide.[1] Since, however, the oils obtained by freezing out the solid hydrocarbons have specific gravities considerably higher than those of the original distillates, and apparently belong to another series, as shown by analysis and refraction indices, it is possible that the solid hydrocarbons held in solution in the oils have their boiling-points depressed in the fractional distillation by which they were separated from the main body of the crude oil. Still, the molecular weights of the solid hydrocarbons correspond to definite formulas; for instance, from the distillate 300°–301°, atmospheric pressure, octodecane was separated in a practically pure form.

The less volatile portions of Pennsylvania petroleum consist of several series of hydrocarbons. The series C_nH_{2n} is liquid even at low temperatures, of higher specific gravity, and another is composed of solid hydrocarbons of the series C_nH_{2n+2}.

In a former paper[2] it was shown that the high values assigned by Pelouze and Cahours as the specific gravity of the distillates separated by them from petroleum, indicated that their hydrocarbons were separated from Canadian petroleum. The same inference is supported by the high specific gravity of the hydrocarbons boiling above 216°, which were separated by Pelouze and Cahours, as compared with the specific gravity of the hydrocarbons, separated from Pennsylvania petroleum, described in this paper.

After establishing a homologous series by analysis, evidently the only means available for Pelouze and Cahours to determine the molecular size of the hydrocarbons was to assume that a hydrocarbon constituted the chief portion of any distillates that collected in unusually large amounts, and to compute the series in unbroken order from the lower members.

Several attempts were made to show the presence of the hydrocarbon $C_{20}H_{42}$, but the distillates between the limits 215°

[1] Ann. Chem. (Liebig), **152**, 15.
[2] Proc. Am. Acad., **32**, 171.

and 225° were small, and in none of them did the molecular weight obtained correspond to this formula.

Heneicosane, $C_{21}H_{44}$, *and Liquid Hydrocarbon*, $C_{21}H_{42}$. *From Distillate 230°–232°, 50 mm.*—Larger quantities of distillates amounting to 200 grams collected at 230° to 232°, for the most part at 230° to 231°. The specific gravity of the unpurified distillate was 0.8321 ; after purification it gave 0.8230. A combustion of the purified oil gave the following percentages of carbon and hydrogen :

0.1540 gram oil gave 0.4813 gram CO_2 and 0.1968 gram H_2O.

	Calculated for		Found.
	$C_nH_{2n}.$	$C_{21}H_{44}.$	
C	85.70	85.14	85.23
H	14.30	14.86	14.32

There was evidently some loss in this analysis, but the percentages are more satisfactory for the formula $C_{21}H_{42}$. It will be shown that this distillate was a mixture of a solid hydrocarbon with an oil of higher specific gravity. Its molecular weight was determined at the freezing-point of benzene.

I. 1.4807 grams oil and 25.9125 grams benzene gave a depression of 0°.949.

II. 0.6845 gram oil and 19.48 grams benzene gave a depression of 0°.579.

Calculated for		Found.	
$C_{21}H_{42}.$	$C_{21}H_{44}.$	I.	II.
294	296	295	297.4

The index of refraction of this hydrocarbon was found to be 1.4608, corresponding to the molecular refraction :

Calculated for	Found.
$C_{21}H_{42}.$	
96.66	96.91

The molecular weight and molecular refraction show that this distillate is composed of a hydrocarbon containing 21 carbon atoms, and the combustion and the high specific gravity point to the series C_nH_{2n}.

A portion of the oil was cooled to —10°, filtered cold, the solid well pressed in filter-paper, and crystallized from ether and alcohol. The ready solubility of these solid hydrocar-

bons in ether and their insolubility in alcohol afford an easy means of purification. The melting-point of the purified solid was 40° to 41°.

A combustion gave the following values for carbon and hydrogen:

0.1353 gram substance gave 0.4237 gram CO_2 and 0.1778 gram H_2O.

	Calculated for $C_{21}H_{44}$.	Found.
C	85.13	85.39
H	14.87	14.72

The filtered oil gave as its specific gravity, at 20°, 0.8424. The percentages of carbon and hydrogen were ascertained by a combustion:

0.1498 gram oil gave 0.4724 gram CO_2 and 0.1898 gram H_2O.

	Calculated for $C_{21}H_{42}$.	Found.
C	85.70	85.98
H	14.30	14.08

Its molecular weight was determined at the freezing-point of benzene.

0.9466 gram oil and 21.01 grams benzene gave a depression of 0°.737.

Calculated for $C_{21}H_{42}$.	Found.
294	299

Docosane, $C_{22}H_{46}$, *and Liquid Hydrocarbon,* $C_{22}H_{44}$. *From Distillate 240°–242°, 50 mm.*—After the thirtieth distillation 150 grams collected at 240° to 242°, which gave as its specific gravity, before purification, 0.8341. After purification with fuming sulphuric acid its specific gravity was 0.8262. Combustions gave the following percentages of carbon and hydrogen:

I. 0.1538 gram oil gave 0.4800 gram CO_2 and 0.1992 gram H_2O.

II. 0.1560 gram oil gave 0.4874 gram CO_2 and 0.2024 gram H_2O.

III. 0.1362 gram oil gave 0.4257 gram CO_2 and 0.1788 gram H_2O.

	Calculated for			Found.	
	$C_{22}H_{44}$.	$C_{22}H_{46}$.	I.	II.	III.
C	85.70	85.16	85.09	85.21	85.25
H	14.30	14.84	14.40	14.42	14.59

The molecular weight was determined as follows:

I. 0.8367 gram oil and 20.38 grams benzene gave a depression of 0°.642.

II. 2.5442 grams oil and 21.91 grams benzene gave a rise in boiling-point of 0°.9566.

Calculated for $C_{22}H_{44}$.	Found.	
	I.	II.
308	313.4	311.3

The index of refraction was found to be 1.454 and the molecular refraction:

Calculated for $C_{22}H_{44}$.	Found.
101.27	100.7

The distillates in the vicinity of 240°, 50 mm., deposited no solid on standing at ordinary temperatures, but higher fractions all deposited solids. When cooled to 0°, the fraction 242°–254° became nearly solid. After further cooling to —10° the solid was filtered in a funnel surrounded with salt and ice, pressed in filter-paper, and crystallized from ether and alcohol. The solid melted at 43°, and when further purified from gasoline, at 44°. Kraft gave 44°.4 as the melting-point of the hydrocarbon $C_{22}H_{46}$. Its specific gravity at 60° was found to be 0.7796. A combustion gave proportions of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1521 gram of the solid gave 0.4721 gram CO_2 and 0.2021 gram H_2O.

	Calculated for		Found.
	$C_{22}H_{44}$.	$C_{22}H_{46}$.	
C	85.70	85.16	85.13
H	14.30	14.84	14.86

The quantity of the hydrocarbon was not sufficient for a determination of its molecular weight.

The filtered oil gave as its specific gravity, at 20°, 0.8296, a value somewhat higher than that obtained before filtration. A combustion gave the following percentages of carbon and hydrogen:

0.1505 gram oil gave 0.4717 gram CO_2 and 0.1937 gram H_2O.

0.1411 gram oil gave 0.4419 gram CO_2 and 0.1819 gram H_2O.

	Calculated for $C_{22}H_{44}$.	I.	II.
C	85.70	85.49	85.41
H	14.30	14.31	14.32

These proportions correspond to the formula $C_{22}H_{44}$, which is supported by the high specific gravity.

The molecular weight of the filtered oil was also determined :

1.0713 grams oil and 19.60 grams benzene gave a depression of 0°.858.

Calculated for $C_{22}H_{44}$.	Found.
308	312

The wide difference in specific gravity between the solid and liquid hydrocarbons which boil at 240° to 242, 50 mm., points to different series. While the percentages of carbon and hydrogen given by analysis could not alone be depended on to prove the different series, the results of combustion with specific gravity are sufficient. The differences in theoretical composition of the two series are 0.5 per cent for carbon and for hydrogen. In combustions conducted under the most favorable conditions and with the greatest care, the different series may be shown in well purified materials. But with so many determinations, and the extreme care in details of the method, while the percentages obtained are sufficiently close to indicate the series, the results are not in all cases as close to the calculated percentages as should be reached in the greater precision of a few analyses.

Tricosane, $C_{23}H_{48}$, *and Liquid Hydrocarbon*, $C_{23}H_{46}$. *From Distillate 258°–260°, 50 mm.*—After the nineteenth distillation, 175 grams collected at 258° to 260°, 50 mm., for the most part at 260° to 261° which deposited a considerable quantity of solid hydrocarbon on standing. The specific gravity of the unpurified distillate decanted from the solid was as follows :

60°, 0.8341 ;   70°, 0.8320 ;   80°, 0.8310.

The oil was agitated several times with concentrated sulphuric acid until the acid was not much colored, and washed with sodium hydroxide and water, and finally with salt brine. On account of the high specific gravity of the oil some heavy solution such as brine or calcium chloride was necessary to separate the water and oil. The oil was dried for examination over calcium chloride and metallic sodium.

The combustion of the oil gave the following percentages of carbon and hydrogen :

0.1508 gram oil gave 0.4711 gram CO_2 and 0.1945 gram H_2O.

	Calculated for		Found.
	$C_{22}H_{46}$.	$C_{23}H_{48}$.	
C	85.70	85.18	85.21
H	14.30	14.82	14.33

A part of the carbon dioxide was evidently lost, but the results point to the series C_nH_{2n}, which represents the composition of the oil, much the larger part of the distillate.

A portion of the distillate was cooled to —10°, and filtered cold to separate the crystalline solid. The solubility of the solid hydrocarbon seemed to diminish rapidly with lower temperatures, consequently a small proportion of the solid remains in the oil below —10°. After pressing and crystallizing from ether and alcohol, the solid melted at 45°. Krafft's hydrocarbon, $C_{23}H_{48}$, melted at 47°.7. Two determinations of its specific gravity, at 60°, gave (1) 0.7894, (2) 0.7900.

A combustion of the solid gave results for the series C_nH_{2n+2}.

0.1515 gram substance gave 0.4710 gram CO_2 and 0.1989 gram H_2O.

	Calculated for $C_{23}H_{48}$.	Found.
C	85.20	85.06
H	14.80	14.64

A determination of its molecular weight at the boiling-point of benzene was made :

1.1208 grams of the substance and 23.08 grams benzene gave a rise of 0°.412.

Calculated for $C_{23}H_{48}$.	Found.
324	327

The filtered oil gave as its specific gravity, at 20°, 0.8569. It gave percentages of carbon and hydrogen required for the series C_nH_{2n} :

0.1504 gram oil gave 0.4711 gram CO_2 and 0.1945 gram H_2O.

	Calculated for $C_{23}H_{46}$.	Calculated for $C_{23}H_{48}$.	Found.
C	85.70	85.18	85.41
H	14.30	14.82	14.36

The molecular weight was determined at the freezing-point of benzene :

3.464 grams oil and 26.06 grams benzene gave a depression of 1°.0475.

Calculated for $C_{23}H_{46}$.	Found.
322	325

The index of refraction was found to be 1.4714, from which was calculated the molecular refraction :

Calculated for $C_{23}H_{46}$.	Found.
105.87	105.31

Tetracosane, $C_{24}H_{50}$, *and Liquid Hydrocarbon,* $C_{24}H_{48}$. *From Distillate 272°–274°, 50 mm.*—After the nineteenth distillation, 150 grams collected at 272° to 274°, 50 mm., that became partly solid on standing. The decanted oil gave as its specific gravity 0.8448, at 20°. A part of the distillate was then cooled to —10°, and the solid filtered cold under pressure.

The distillate was purified by treatment with successive portions of fuming sulphuric acid until the acid was nearly colorless, then washed with sodium hydroxide and a concentrated solution of calcium chloride, and dried over fused calcium chloride and sodium. Nearly one-third of the volume was removed in purification. The purified oil then gave as its specific gravity, at 20°, 0.8598, and at higher temperatures :

60°, 0.8375 ;   70°, 0.8366 ;   80°, 0.8354.

A combustion of the purified oil gave percentages of carbon and hydrogen required for the series C_nH_{2n}.

0.1539 gram oil gave 0.4769 gram CO_2 and 0.2000 gram H_2O.

	Calculated for $C_{24}H_{48}$.	$C_{24}H_{50}$.	Found.
C	85.70	85.21	85.35
H	14.30	14.79	14.54

These percentages evidently support the formula $C_{24}H_{48}$.

A determination of the molecular weight of the liquid hydrocarbon gave at the boiling-point of benzene a result required for $C_{24}H_{48}$.

2.0681 grams oil and 25.78 grams benzene gave a rise of 0°.6096.

Calculated for $C_{24}H_{48}$.	Found.
336	337.4

The index of refraction of the oil was found to be 1.4726, from which the following molecular refraction was calculated :

Calculated for $C_{24}H_{48}$.	Found.
110.47	109.75

Specific gravity of the oil at $\frac{20°}{4°}$, 0.8582.

The solid separated by filtration melted at 48°. Krafft's hydrocarbon, $C_{24}H_{48}$, melted at 51°. It gave as its specific gravity the following values :

60°, 0.7902 ;   70°, 0.7893 ;   80°, 0.7875.

Compared with water at 4°, these results reduce to 0.7742. The specific gravity given by Krafft to tetracosane, at 4°, was 0.7784, the same as that of the solid hydrocarbon which he separated from shale oil. The solid products from Pennsylvania oil show only slight variations in specific gravity. But the heavy oils show a decided increase in specific gravity with increase in molecular weight.

A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1433 gram of the solid gave 0.4479 gram CO_2 and 0.1895 gram H_2O.

	Calculated for		
	C_nH_{2n}.	$C_{24}H_{50}$.	Found.
C	85.70	85.23	85.25
H	14.30	14.77	14.70

The molecular weight was determined at the boiling-point of benzene.

Calculated for $C_{24}H_{50}$.	Found.
338	337

To ascertain whether the solid which separated at ordinary temperatures was identical with what remains in solution, a portion of the oil was cooled to 0°, filtered at the same temperature, and the filtrate cooled to —10° and filtered under pressure at the same temperature. The three solids were carefully purified by crystallization from ether and alcohol, and their melting-points taken. The solid separated at ordinary temperatures melted at 48°, that separated at 6° melted at 51° to 52°, and that separated at —10° melted at 51° to 52°.

It is therefore evident that this distillate consists chiefly of one solid hydrocarbon, $C_{24}H_{50}$, and that the oil remaining liquid at —10° belongs to a different series.

Pentacosane, $C_{25}H_{52}$, *and Liquid Hydrocarbon*, $C_{26}H_{52}$. *From Distillate 280°–282°, 50 mm.*—After the fifteenth distillation, 100 grams collected at 280° to 282°, 50 mm., which deposited a larger quantity of solid hydrocarbon than the lower distillates. This solid was separated from the oil and the latter was then cooled to 0° and filtered at the same temperature.

The specific gravity of the filtered oil at 20° was 0.8580.

A combustion gave the following values :

0.1593 gram oil gave 0.4997 gram CO_2 and 0.2107 gram H_2O.

	Calculated for $C_{26}H_{52}$.	Found.
C	85.70	85.55
H	14.30	14.67

The formula was established by its molecular weight, determined at the boiling-point of benzene.

3.9867 grams oil and 30.19 grams benzene gave a rise of 0°.936.

Calculated for $C_{26}H_{52}$.	Found.
364	362

A determination of the index of refraction gave 1.4725, which corresponded to the molecular refraction :

Calculated for $C_{26}H_{52}$.	Found.
119.87	119.12

After crystallization from ether and alcohol, from which it separated in crystalline plates, the solid hydrocarbon gave percentages of carbon and hydrogen required for the series C_nH_{2n+2}.

0.1534 gram substance gave 0.4787 gram CO_2 and 0.2006 gram H_2O.

	Calculated for $C_{25}H_{52}$.	Found.
C	85.25	85.09
H	14.75	14.53

A determination of its molecular weight verified the formula.

1.7583 grams substance and 24.39 grams benzene gave, by the boiling-point method, a rise of 0°.5231.

Calculated for $C_{25}H_{52}$.	Found.
352	353.4

Melting-point of the solid hydrocarbon, 53° to 54°.

Hexacosane, $C_{26}H_{54}$, *and Liquid Hydrocarbon,* $C_{27}H_{52}$. *From Distillate 292°–294°, 50 mm.*—After the fifteenth distillation, 100 grams collected at 292° to 294°, 50 mm., which deposited a considerable quantity of solid crystalline hydrocarbon. These crystals were filtered, pressed, and purified by crystallization from ether and alcohol. Melting-point, 58°. The specific gravity of this hydrocarbon was determined as follows :

60°, 0.7977 ;   70°, 0.7956 ;   80°, 0.7943.

A combustion of the solid gave the following percentages of carbon and hydrogen :

0.1508 gram substance gave 0.4709 gram CO_2 and 0.2033 gram H_2O.

	Calculated for $C_{26}H_{54}$.	Found.
C	85.24	85.17
H	14.76	14.98

The molecular weight was ascertained at the boiling-point of benzene.

1.2754 grams substance and 24.2827 grams benzene gave a rise of 0°.416.

Calculated for $C_{26}H_{54}$.	Found.
366	364

On cooling the original distillate to —10°, it formed a thick, pasty mass. It was filtered under pressure, keeping cold. The filtered crystals were pressed and crystallized from ether and alcohol. Melting-point, 58°. The solids pressed out from the fractions from 288° to 302°, 50 mm., showed very slight variations in melting-points.

288°–290°, 56°. 300°–304°, 59°–60°.
294°–296°, 58°. 302°–304°, 59°–60°.

The oil filtered under pressure was very thick and viscous. Its specific gravity, at 26°, was 0.8688. A combustion gave the following percentages of carbon and hydrogen :

0.1500 gram oil gave 0.4750 gram CO_2 and 0.1812 gram H_2O.

	Calculated for $C_{27}H_{52}$.	Found.
C	86.17	86.36
H	13.83	13.43

The molecular weight at the boiling-point of benzene corresponded to the formula $C_{27}H_{52}$.

3.6506 grams oil and 25.80 grams benzene gave a rise of 0°.964.

Calculated for $C_{27}H_{52}$.	Found.
376	376.2

The index of refraction corresponded to the same formula.

The index was found to be 1.4722, and the molecular refraction :

Calculated for $C_{27}H_{52}$.	Found.
122	121.4

Octocosane, $C_{28}H_{58}$, *and Liquid Hydrocarbon*, $C_{28}H_{54}$. *From Distillate 310°–312°, 50 mm.*—After the tenth distillation 75 grams collected at 310° to 312°, from which a considerable quantity of crystals collected above the oil on standing. The oil separated from the crystals was then cooled to —10° and filtered cold under pressure. The solid was pressed and purified by crystallization from ether and alcohol. Melting-point, 60°. Its specific gravity was determined as follows :

70°, 0.7945 ;   80°, 0.7927 ;   90°, 0.7911.

A combustion gave the following percentages of carbon and hydrogen :

0.1508 gram substance gave 0.4703 gram CO_2 and 0.2032 gram H_2O.

	Calculated for $C_{28}H_{58}$.	Found.
C	85.28	85.07
H	14.72	14.97

The molecular weight at the boiling-point of benzene corresponded to the formula $C_{28}H_{58}$.

3.070 grams solid hydrocarbon and 26.21 grams benzene gave a rise of 0°.7538.

Calculated for $C_{28}H_{58}$.	Found.
394	399

A very thick oil, separated by filtration, gave as its specific gravity, at 20°, 0.8694. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}.

0.1500 gram oil gave 0.4729 gram CO_2 and 0.1836 gram H_2O.

	Calculated for			Found.
	$C_{28}H_{58}$.	$C_{28}H_{56}$.	$C_{28}H_{54}$.	
C	85.28	85.70	86.02	85.96
H	14.72	14.30	13.98	13.60

The molecular weight was found at the boiling-point of benzene.

I. 2.6792 grams oil and 29.85 grams benzene gave a rise of 0°.5826.

II. 1.9196 grams oil and 27.98 grams benzene gave a rise of 0°.4459.

Calculated for $C_{28}H_{54}$.	Found.	
	I.	II.
392	396	394.4

The index of refraction was found to be 1.480, which corresponds to the molecular refractions :

Calculated for $C_{28}H_{54}$.	Found.
127	126.78

It will be observed that the two liquid hydrocarbons last described have been shown to belong to a series C_nH_{2n-2}. Results already obtained, but not yet published, indicate that the same series of hydrocarbons constitute the less volatile portions of Canadian petroleum, and probably also of Ohio petroleum. Results already published show that the less volatile distillates from California and Texas petroleum are composed of the same series and other series still poorer in hydrogen.

The unexpected appearance of the series C_nH_{2n-2} in Pennsylvania petroleum suggests a closer relationship between this petroleum and the heavier oils from other fields, such as those in Texas and California, than was suspected. To gain further information concerning the heavier portions of Pennsylvania oil, we allowed 3 kilograms of the sample from which the hydrocarbons described in this paper were prepared, to evaporate spontaneously in the air in a strong draught, but with no application of heat. At the end of thirty days there remained 1 kilogram that gave as its specific gravity 0.8620, practically the same as that of $C_{28}H_{54}$, 0.8694. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2}. A distillation showed that 65 per cent of the residual oil was composed of hydrocarbons above $C_{15}H_{30}$. The composition of these hydrocarbons will be ascertained in connection with the study of natural and commercial paraffin, which is now in progress.

This interesting relation, and others between the numerous petroleums from different oil fields that have been examined in this laboratory, will be presented more at length in a later paper.

As a general summary of the results described in this paper, hydrocarbons have been identified as shown in the following table.

It appears that the liquid hydrocarbon, $C_{28}H_{54}$, in fraction 310°–312°, has the same number of carbon atoms as the solid hydrocarbon octosane in the same fraction. In this respect the hydrocarbons in this fraction differ from those in the two preceding fractions, in each of which the liquid hydrocarbon has one more carbon atom than the solid constituent. Determinations of the molecular weights of hydrocarbons with high carbon content can only be made by the boiling-point method; and even with the greatest care in manipulation this method is somewhat uncertain for high molecular weights of solid hydrocarbons, for the reason that the rise in boiling-points diminishes with the increase in molecular weight. With oils there is less difficulty. For instance, the molecular weight, 376.2, of the liquid hydrocarbon $C_{27}H_{52}$, given on page 194, is one of five closely concordant determinations by different persons. As an illustration of the care necessary in details, heating with a lamp supplied with gas from the laboratory mains is so irregular on account of variation in gas pressure that the gas must be supplied from a tank under water pressure.

Name.	Symbol.	Boiling-point.	Melting-point.
Tridecane	$C_{13}H_{28}$	226°	
Tetradecane	$C_{14}H_{30}$	236°–238°	
Pentadecane	$C_{15}H_{32}$	256°–257°	
Hexadecane	$C_{16}H_{34}$	274°–275°	
Heptadecane	$C_{17}H_{36}$	288°–289°	10°
Octodecane	$C_{18}H_{38}$	300°–301°	20°
Nonodecane	$C_{19}H_{40}$	210°–212°, 50 mm.	33°–34°
Heneicosane	$C_{21}H_{44}$	230°–231° "	40°–41°
Hydrocarbon, liquid at –10°	$C_{22}H_{44}$	240°–242° "	
Docosane	$C_{22}H_{46}$		44°
Hydrocarbon, liquid at –10°	$C_{23}H_{46}$	258°–260° "	
Tricosane	$C_{23}H_{48}$		45°
Hydrocarbon, liquid at –10°	$C_{24}H_{48}$	272°–274° "	

Name.	Symbol.	Boiling-point.	Melting-point.
Tetracosane	$C_{24}H_{50}$		48°
Hydrocarbon, liquid at −10°	$C_{24}H_{52}$	280°–282° 50 mm.	
Pentacosane	$C_{25}H_{52}$		53°–54°
Hydrocarbon, liquid at −10°	$C_{27}H_{52}$	292°–294° "	
Hexacosane	$C_{26}H_{54}$		58°
Hydrocarbon, liquid at −10°	$C_{28}H_{54}$	310°–312° "	
Octocosane	$C_{28}H_{58}$		60°

Much attention has been given to these determinations, especially by Messrs. O. J. Sieplein and R. P. Cushing.

The preparation of the distillates described in this paper was begun December 1, 1896, by Mr. A. S. Kittelberger, who distilled 56 kilograms of Pennsylvania crude oil. The distillations were later continued by different assistants. The following gentlemen have also aided in the purification, examination, and analysis of these hydrocarbons: Messrs. Shaw, Latimer, R. P. Cushing, Dr. E. J. Hudson, and O. J. Sieplein. To the latter especially is due the analysis and identification of the chlorine derivatives of the hydrocarbons.

ON SOME HYDROXYLAMINE COMPOUNDS.[1]

By Maxwell Adams.

As a reagent in organic chemistry hydroxylamine has been carefully investigated, but from the standpoint of inorganic chemistry it has not received much attention, and the investigations in this field are in many places incomplete or contradictory. One reason for this neglect has been the cost and trouble of preparing it by the ordinary methods. These difficulties have now been overcome by the very economical and satisfactory method of Divers and Haga.[2]

The results obtained by Hofmann,[3] Rammelsberg,[4] and Pesci,[5] on the mercuramines, indicate a parallel line of work

[1] The author's inaugural dissertation submitted to the faculties of the Graduate Schools of Arts, Literature, and Science of the University of Chicago, in candidacy for the degree of Doctor of Philosophy.

[2] J. Chem. Soc. (London), **69**, 1665.

[3] Ann. Chem. (Liebig), **305**, 191.

[4] J. prakt. Chem., **38**, 558.

[5] Ztschr. anorg. Chem., **21**, 361.

with hydroxylamine because of its relationship to ammonia.

The similarity of hydroxylamine to both water and ammonia indicates that through a study of it as a solvent some light might be thrown upon the part played by these liquids in crystallization. Pure hydroxylamine is a liquid above 33°; it might be used as a solvent in determining the electrolytic conductivity of solutions, and it would be interesting to note if it resembles water or ammonia in this particular.

The consideration of these facts, among others, led Dr. Lengfeld to suggest to me a study of hydroxylamine as a promising field for work. A review of the methods of preparation and estimation of hydroxylamine, its action on salts of mercury, and the properties of some of its halogen salts which have been hitherto overlooked, are considered in this article.

When the study was begun many conflicting statements were found, and it at once became evident that much work needed repetition, and a not inconsiderable part of this paper is devoted to a review of previous work. Attention was first directed towards the methods ordinarily used in the estimation of hydroxylamine; these were found inaccurate, and before any progress in this work could be made they had to be revised. Volumetric methods for the determination of hydroxylamine were first carried out in a systematic manner by Meyeringh,[1] who recommended three different processes :

1. The reduction of ferric sulphate with hydroxylamine and estimation of the ferrous sulphate with potassium permanganate.

2. The reduction of Fehling's solution.

3. The titration with free iodine solution in the presence of sodium phosphate or sodium bicarbonate.

All these methods have been employed by various chemists, some recommending one and some another. Knorre and Arndt,[2] in their work on the oxidation-products of hydroxylamine, use permanganate, and Lainer,[3] in his photographic work with hydroxylamine, employs the same reagent. This method was tested and found to be inaccurate. The amount

[1] Ber. d. chem. Ges., **10**, 1940.
[2] *Ibid.*, **33**, 30.
[3] Dingler : Polytech. J., **276**, 521.

of permanganate necessary for the titration was found to vary with the amount of ferric sulphate present, the length of time the solution was heated with the hydroxylamine, and the rapidity with which the permanganate was added.

Titration with free iodine in the presence of bicarbonate of sodium is used by Haga,[1] but this method has some defects. He finds that extreme dilution, or presence of carbonic acid, brings the results too high. The presence of other salts also influences the accuracy. In the present work the best results were obtained by titrating with standard iodine solution in the presence of sodium phosphate. When too great dilution is avoided and the relative proportions of the hydroxylamine and the sodium phosphate are kept fairly constant, concordant results are obtained. Wherever it was possible, however, the hydroxylamine was calculated indirectly from the nitrogen, which was determined by the Dumas method. The titration method was used to prove only that the nitrogen is not present as ammonia.

The behavior of mercury salts towards hydroxylamine was first investigated by Dresler and Stein,[2] who tried the action of hydroxylamine on mercuric oxide and obtained free mercury, and Lossen,[3] who found that mercuric chloride was rapidly reduced by the same means. There is no doubt that this is true under certain conditions, but by varying the temperature and solvent several compounds of mercury with hydroxylamine may be obtained. A salt,

$$HgSO_4.(NH_2OH)_2.H_2O,$$
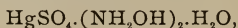
prepared by the action of hydroxylamine on mercuric sulphate, corresponds closely to the salts of cobalt, manganese, and nickel prepared by Feldt[4] and Uhlenhuth.[5] The chlorides of hydroxylamine and mercury, on the other hand, seem, as a rule, more complex. Crismer[6] and other chemists have prepared chlorides of zinc, cadmium, barium, cobalt, and manganese with hydroxylamine of crystallization. These com-

[1] J. Chem. Soc. (London), **51**, 794.
[2] Ann. Chem. (Liebig), **150**, 242.
[3] *Ibid.*, Supp.-Bd., **6**, 220.
[4] Ber. d. chem. Ges., **27**, 401.
[5] Ann. Chem. (Liebig), **307**, 332.
[6] Bull. Chem. Soc., [3], **3**, 114.

pounds have the general formula $MCl_2(NH_2OH)_2$. Feldt,[1] in his effort to prepare the corresponding salt of mercury confirmed the statement of Lossen, Dressler, and others, that on account of the reducing action of hydroxylamine and the easy reduction of mercuric chloride, no stable addition-product is obtained. By modifying conditions of temperature and solvent, however, I have prepared and isolated a number of chlorides of mercury and hydroxylamine. The simplest of these, $HgCl_2(NH_2OH)_2$, corresponds in composition to the general type of the chlorides mentioned above. Further work, however, may show that it is analogous to the mercuramines. It forms a double salt with normal hydroxylamine hydrochloride, $HgCl_2.(NH_2OH)_2(NH_2OH.HCl)_2$, and also a double salt with dibasic hydroxylamine hydrochloride,

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl.$$
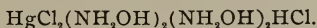
Besides these, a double salt of mercuric chloride with normal hydroxylamine hydrochloride, $HgCl_2(NH_2OH)HCl$, has been obtained, as well as a stable compound which may be mercuric chloride with dibasic hydroxylamine hydrochloride, $2HgCl_2.5(NH_2OH)_2HCl$, though it is probably much more complex.

Thinking that the other halogen salts of mercury and hydroxylamine might be less complex, I attempted to prepare them, but no compound with mercury and iodine was obtained, and only one bromide,

$$HgBr_2(NH_2OH)_2(NH_2OH.HBr)_2,$$
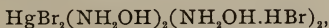
was prepared. The hydrobromide and hydriodide of hydroxylamine have a stronger reducing action upon mercury than the corresponding chloride, and they also appear to have less tendency to form complex salts. While Lossen[2] made a number of salts of hydroxylamine, and other chemists have since added to the number, no account of the hydrobromide has been given. Piloty and Ruff[3] prepared the tribasic hydroxylamine hydriodide, and Dunstan and Golding[4] made

[1] *Loc. cit.*
[2] Ann. Chem. (Liebig), Supp.-Bd., **6**, 220.
[3] Ber. d. chem. Ges., **30**, 1656.
[4] J. Chem. Soc. (London), **69**, 839.

the dibasic hydriodide, but they were unable to obtain the normal hydriodide. I have prepared both the normal, $NH_2OH.HBr$, and the dibasic, $(NH_2OH)_2HBr$, hydroxylamine hydrobromides as well as the normal hydroxylamine hydriodide, $NH_2OH.HI$. As no double bromides or iodides of hydroxylamine with metallic salts corresponding to the general formula, $MX_2(NH_2OH)_2$, had been prepared, and since their action on mercury is too violent to separate any intermediate products of the reaction, it seemed desirable to study the action of hydroxylamine hydriodide and hydrobromide on cadmium salts, which, though similar to those of mercury, are less easily reduced. The compounds $CdBr_2(NH_2OH)_2$ and $CdI_2(NH_2OH)_3$ were readily obtained from this reaction.

Many experiments in this work required the use of pure, dry hydroxylamine. This was made from the phosphate by distillation according to the method of Uhlenhuth.[1]

<div align="center">EXPERIMENTAL PART.</div>

Hydroxylamine sulphate, the starting point in the preparation of all the salts described below, is made according to the directions of Divers and Haga.[2] The following slight modifications, however, are observed in carrying out their method :

1. A constant supply of gas for sulphonating is obtained by using liquid sulphur dioxide confined in siphons.

2. If the solution into which the sulphur dioxide is being led contains 2 or less molecules of sodium carbonate to 1 molecule of sodium nitrite, the entire solution may decompose toward the end of the reaction, even though the vessel containing the solution is immersed in brine and ice. To avoid this a solution containing sodium carbonate in slight excess of the molecular proportions is employed. It was also found that, even if by mistake too little sodium carbonate has been added at the beginning, the decomposition could be arrested, if, as soon as the solution began to turn brown, sodium carbonate was added and sulphur dioxide run in until the solution became colorless. Taking these precautions the solution remains clear when it becomes acid, and may be warmed up rapidly with perfect safety.

[1] Ann. Chem. (Liebig), **311**, 117.
[2] *Loc. cit.*

3. After hydrolysis of the sodium oxamidosulphonate, $NH(OH)(SO_3Na)$, and the neutralization of the resulting sulphuric acid with sodium carbonate, it was found convenient to first cool the solution to zero and separate the principal portion of the sodium sulphate by crystallization, then to evaporate the remaining solution to such a volume that 1 cc. contains 0.25 gram of hydroxylamine sulphate, finally to cool this solution to —8°, and to remove the sodium sulphate which crystallizes. By this separation of the sodium sulphate into two portions the bulk of the solution is quickly reduced, the first and largest yield of sodium sulphate crystals is easily separated from hydroxylamine, and a concentrated solution of hydroxylamine sulphate is obtained which may be cooled to —8° without freezing.

4. The final concentration of the solution containing the hydroxylamine sulphate is carried out at diminished pressure, thereby avoiding local superheating and decomposition.

Dry hydroxylamine sulphate is insoluble in absolute alcohol and almost insoluble in 95 per cent alcohol.

As in the course of this work it was necessary to know approximately the solubility of hydroxylamine sulphate in water at various temperatures, the following table, giving the amount of hydroxylamine sulphate in 1 gram water solution, was worked out ; absolute accuracy was not attempted :

Temperature.	Grams of hydroxylamine sulphate.
—8°	0.307
0	0.329
10	0.366
20	0.413
30	0.441
40	0.482
50	0.522
60	0.560
90	0.685

Hydroxylamine Phosphate.—The phosphate of hydroxylamine is about one-twentieth as soluble in water at the ordinary temperature as the sulphate ; hence when normal sodium phosphate is added to a concentrated solution of hydroxylamine sulphate, the phosphate separates in crystalline form,

and it can be readily purified by recrystallization. Its solubility in water is as follows, the amount of the salt in 1 gram of the water solution being given :

Temperature.	Grams of hydroxylamine phosphate.
0°	0.012
10	0.015
20	0.019
30	0.027
40	0.040
50	0.055
60	0.077
70	0.102
80	0.133
90	0.168

The difference in solubility between the phosphate and sulphate may be utilized to work up the mother-liquor and wash-waters from which the sulphate will no longer crystallize.

In the preparation of the sulphate by the Divers and Haga method, after two or three crops of crystals have been separated, there remains a viscous mother-liquor containing considerable hydroxylamine sulphate mixed with sodium sulphate, with impurities which were contained in the original crude materials, and with decomposition-products formed during the hydrolysis. From this mixture normal sodium phosphate precipitates a considerable amount of hydroxylamine phosphate.

The normal sodium phosphate for this purpose is readily prepared by adding the calculated quantity of sodium hydroxide to acid sodium phosphate. Including both the sulphate and phosphate, the yield of hydroxylamine obtained by this method is even better than that reported by Divers and Haga. Nine hundred grams of sodium nitrite gave 700 grams of sulphate and 80 grams of phosphate of hydroxylamine.

Hydroxylamine Hydrochloride, $NH_2OH.HCl$. — Eickhoff[1] states that if the calculated quantity of barium chloride be added to hydroxylamine sulphate in water solution and the barium sulphate removed by filtration, the hydroxylamine hydrochloride may be separated by concentration and crystal-

[1] J. Pharm., [5], **21**, 245-246; Abstr. in J. Chem. Soc. (London), **58**, 558 (1890).

lization. This method is difficult to carry out and the yield is poor. When either reagent is in excess double salts are formed, and if the hydroxylamine sulphate contains any impurities it is not easy to calculate the exact quantity of the chloride required for neutralization.

The following modification of the process is found to be much more satisfactory : Barium chloride is added in slight excess to a water solution of hydroxylamine sulphate, the solution filtered free from barium sulphate, and evaporated to dryness on a water-bath. The residue is placed in a Soxhlet apparatus and extracted with alcohol, the insoluble barium chloride remaining in the apparatus. The hydroxylamine hydrochloride, being only moderately soluble in alcohol, soon crystallizes in the distilling-flask, and that remaining in solution is easily obtained by evaporating the alcohol.

If chemically pure hydrochloride is desired, absolute alcohol should be used, taking precautions to exclude moisture, but for most purposes 95 per cent alcohol is satisfactory. The hydrochloride obtained in this way contains only a slight trace of barium. The phosphate being relatively insoluble in water can be easily purified by crystallization, and is also converted into the hydrochloride by the above process. This method is found convenient for reclaiming residues of hydroxylamine and reconverting them into the hydrochloride.

Hydroxylamine Hydrobromide, $NH_2OH.HBr$.—This salt is obtained as follows : Barium bromide is added to hydroxylamine sulphate in water solution, keeping the sulphate in slight excess, as barium bromide is not insoluble in alcohol. After filtering, the solution is evaporated to dryness on the water-bath, the residue dried in a vacuum desiccator over calcium chloride for forty-eight hours and extracted with absolute alcohol. On cooling the solution, large, well-formed, white, acicular crystals of hydroxylamine hydrobromide are deposited. A further yield of the salt is obtained, either by evaporating the alcoholic solution or by precipitating with ether. When the hydrobromide is precipitated from its alcoholic solution by ether, the crystals formed are shorter and the bases more prismatic than when crystallized by evapora-

tion. This salt is very soluble in water, insoluble in ether; pure and dry it is stable if kept in glass-stoppered bottles. In the presence of impurities it decomposes slowly in the light, becoming yellowish-brown in color. It is a stronger reducing agent than the corresponding hydrochloride.

I. 5 cc. solution containing 0.03135 gram substance required 6.8 cc. standard iodine solution (1 cc. iodine solution equals 0.00133 gram hydroxylamine).

II. 0.2913 gram substance gave 0.4799 gram AgBr and 0.0627 gram gave, on titration, 0.0182 gram hydroxylamine.

	Calculated for $NH_2OH.HBr.$	Found. I.	Found. II.
Br	70.17	....	70.09
NH_2OH	29.02	28.86	28.92

Dibasic Hydroxylamine Hydrobromide, $(NH_2OH)_2HBr$.— This salt is prepared by adding free hydroxylamine to a concentrated alcoholic solution of the normal hydroxylamine hydrobromide. It separates as well-formed, white, plate-like crystals. A second crop of crystals separates upon the addition of a little ether to the filtrate. This compound is less soluble in alcohol at ordinary temperature than the normal salt. It is insoluble in ether and ligroin, very soluble in water. It acts as a strong reducing agent, and under normal conditions its properties are very similar to those of the corresponding dibasic hydrochloride. Analysis shows it to be $(NH_2OH)_2.HBr$.

0.2065 gram substance gave 0.2671 gram AgBr.

0.0513 gram required 17.3 cc. iodine solution.

	Calculated for $(NH_2OH)_2.HBr.$	Found.
Br	54.42	54.54
NH_2OH	44.89	44.87

Various proportions of free hydroxylamine were added to solutions of normal hydroxylamine hydrobromide in water and alcohol in an effort to prepare salts corresponding to the tribasic hydrochloride described by Lossen,[1] and the tribasic hydriodide prepared by Piloty and Ruff,[2] but without success.

[1] Ztschr. Chem. (N. F.), **7**, 326.
[2] *Loc. cit.*

Hydroxylamine Hydriodide, NH$_2$OH.HI.—Dunstan and Golding[1] obtained the dibasic and tribasic hydroxylamine hydriodide by the action of methyl iodide on hydroxylamine dissolved in methyl alcohol. They also prepared both these salts by the direct combination of hydroxylamine and hydriodic acid, but when they attempted to prepare the normal hydriodide by mixing the calculated quantity of an alcoholic solution of hydroxylamine with aqueous hydriodic acid, the solution quickly darkened in color, and when it was evaporated either by heating it or by placing it in a desiccator over sulphuric acid, further decomposition occurred. Several other methods for preparing the hydriodide were tried by them without success.

Wolfenstein and Groll[2] have succeeded in making the normal hydriodide by treating free hydroxylamine with a water solution of hydriodic acid and evaporating the solution under diminished pressure. Their method was published after my work was done and it is, I believe, less satisfactory than mine, both as to the ease with which the operation is carried out and also in the yield obtained.

Normal hydroxylamine hydriodide is made by treating a solution of hydriodic acid in dry, low-boiling ligroin with pure hydroxylamine. Ligroin is chosen for this purpose as hydriodic acid attacks alcohol and ether. In making the hydriodic acid by the Lothar Meyer[3] method much time may be saved by keeping the flask containing the moistened iodine in ice-water while the phosphorus is being added. The addition of the phosphorus, which by the old method required a half hour or more, may in this way be accomplished in a few minutes. After the phosphorus is added the mixture is warmed to 40° or 45°, when a steady stream of gaseous hydriodic acid is evolved. This gas is thoroughly dried over calcium iodide[4] and phosphorus pentoxide, then conducted into dry ligroin at zero. On adding dry hydroxylamine to this solution, a violent reaction takes place and there is imme-

[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **34**, 2417.

[3] *Ibid.*, **20**, 3381.

[4] If calcium chloride is used as a drying agent, hydrochloric acid is found in the ligroin solution.

diately formed a white, crystalline precipitate of normal hydroxylamine hydriodide.

A direct analysis of the salt was not made, but after washing it thoroughly with ligroin it was dissolved in water and the proportion of the iodine to the hydroxylamine was found to be 1 molecule of hydroxylamine to 0.996 atom of iodine, which corresponds to the formula $NH_2OH.HI$ of the normal hydriodide.

10 cc. of a solution of the substance gave 0.7516 gram AgI, and 10 cc. of the same solution required 80.2 cc. iodine solution.

At the summer temperature this salt is very unstable, decomposing slowly under dry ligroin; even when placed over calcium chloride it gives off hydriodic acid and turns brown. It takes up moisture from the air and liquefies in a short time. Its water solution almost immediately turns light yellow in color because of a slight decomposition. It dissolves somewhat in ether, but the solution soon becomes cloudy and deposits dibasic hydroxylamine hydriodide. This reaction takes place much more rapidly if the hydroxylamine hydriodide is first dissolved in alcohol and ether is then added to the solution. When treated in this way, well-formed crystals of the dihydroxylamine hydriodide separate immediately and the solution becomes light-yellow in color. When free hydroxylamine is treated with a solution of ethyl iodide made by passing dry hydriodic acid into ether, according to the method of Silva,[1] there is formed dihydrohydroxylamine hydriodide with a considerable quantity of the tribasic hydriodide.

An attempt was made to prepare the normal hydroxylamine hydriodide by treating hydroxylamine sulphate in water solution with barium iodide, following out a method analogous to that by which the hydrochloride and hydrobromide have been prepared, but without success. The color and properties of the solution indicate that the salt was formed, yet when the solution was evaporated, either on the water-bath or under diminished pressure, it became dark in color, and when it was brought finally to dryness there remained free iodine mixed with crystals of some substance that was apparently the di-

[1] J., (1875), p. 250.

hydroxylamine hydriodide.[1] Not much work was done on this as the other method is much more satisfactory.

Sulphate of Mercury and Hydroxylamine,
$HgSO_4(NH_2OH)_2H_2O$.—This salt is prepared by two methods :

1. To freshly precipitated mercuric oxide, washed free from alkali, hydroxylamine sulphate is added in considerable excess. When the mixture is vigorously shaken, the mercuric oxide dissolves entirely, producing a clear solution from which crystals soon separate. Care is taken to keep the solution cold and to avoid an excess of mercuric oxide.

2. To dry mercuric sulphate a 10 per cent solution of hydroxylamine sulphate in water is added and this mixture vigorously agitated, and then rapidly decanted from any undissolved mercuric sulphate. The clear liquid yields, on standing, crystals of the same salt as those made from the mercuric oxide. The crystals obtained by either of the above methods are purified by washing repeatedly with water acidified with sulphuric acid, and dried over phosphorus pentoxide.

Properties.—The salt is decomposed even in the cold by water, first turning a reddish-yellow and finally black. It may be kept in a desiccator over sulphuric acid, in the dark, for some time without undergoing any apparent change, but becomes colored upon exposure to light. When cold, it keeps under a solution containing a little free sulphuric acid or hydroxylamine sulphate, but when warmed to $55°$ it decomposes rapidly.

I.   0.3732 gram substance gave 0.1963 gram Hg.
      0.2750 gram substance gave 0.1700 gram $BaSO_4$.
      0.4387 gram substance gave 29 cc. N at $22°$ and 731.1 mm. (corr.)[2].

II. 0.4886 gram substance gave 0.2556 gram Hg.
      0.4519 gram substance gave 0.2774 gram $BaSO_4$.

[1] The work described here was carried on during the month of July, when the temperature was between 30° and 40° and the atmosphere almost saturated with water vapor. In evaporating at diminished pressure a temperature below 30° was not obtained. The method is similar to that successfully employed by Wolfenstein and Groll.

[2] Corrected for vapor-tension over 30 per cent caustic potash.

0.3812 gram substance gave 24 cc. N at 22° and 732.2 mm. (corr.).

III. 0.4705 gram substance gave 0.2467 gram Hg.
0.1822 gram substance gave 0.1117 gram BaSO$_4$.

	Calculated for HgSO$_4$(NH$_2$OH)$_2$.H$_2$O.	I. Made from oxide.	Found. II.	III. Made from sulphate.
Hg	52.63	52.57	52.51	52.41
SO$_4$	25.26	25.48	25.29	25.28
N	7.36	7.36	7.09	....

Chlorides of Mercury and Hydroxylamine, HgCl$_2$(NH$_2$OH)$_2$. —The compound HgCl$_2$(NH$_2$OH)$_2$ is prepared by the following methods:

1. A cold alcoholic solution of hydroxylamine is added, drop by drop, to a thoroughly agitated solution of mercuric chloride in absolute alcohol, which is cooled to —10°.

2. Free hydroxylamine is added, drop by drop, to a mixture of 4 parts of mercuric chloride and 1 part hydroxylamine hydrochloride, dissolved in alcohol, which is cooled to —10°.

On allowing the solutions produced by either of the above methods to remain cold for a few minutes, white microscopic crystals of HgCl$_2$(NH$_2$OH)$_2$, mixed with mercurous chloride and double salts of HgCl$_2$(NH$_2$OH)$_2$ with hydroxylamine hydrochloride, separate. By filtering, washing, and redissolving in absolute alcohol, to which has been added a trace of hydroxylamine hydrochloride, long, white, acicular crystals of HgCl$_2$(NH$_2$OH)$_2$ are obtained. The second of the above methods gives the better results, as there is less mercurous chloride formed.

I. 0.2152 gram substance gave 0.1290 gram Hg.
0.2977 gram substance gave 0.2495 gram AgCl.
0.3453 gram substance gave 23.8 cc. N at 17° and 735.2 mm. (corr.).

II. 0.0945 gram substance gave 0.0560 gram Hg.
0.1718 gram substance gave 0.1467 gram AgCl.
0.2054 gram substance gave 15 cc. N at 18° and 740.2 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2$.	Found.	
		I. Salt made by 1st method.	II. Salt made by 2nd method.
Hg	59.34	59.98	59.25
Cl	21.06	20.97	21.11
N	8.39	7.97	8.21

This substance is fairly soluble in methyl or ethyl alcohol, from which solution it may be precipitated by ether. On standing in absolute alcohol there is considerable reduction even in the cold, while on warming the reduction is much more rapid. The stability of this salt is increased by the presence of a small quantity of hydroxylamine hydrochloride. Sodium hydroxide decomposes it rapidly. It is insoluble in ether, but readily soluble in a water solution of hydroxylamine hydrochloride, with which it probably forms a double salt. It is immediately decomposed by water into mercurous chloride. The crystals keep their shape, although, under a microscope, they are found to be lusterless and porous. When fresh crystals of this substance are dissolved in alcohol or a water solution of hydroxylamine hydrochloride, and ammonia is added to the solution, a white precipitate is formed which becomes black on standing a few minutes in the cold, or immediately on warming. This change of color is accompanied by an evolution of gas, and finally gray metallic mercury collects.

$HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.—One molecule of mercuric chloride and 2 molecules of hydroxylamine hydrochloride are dissolved in absolute methyl alcohol, cooled down to —10°, and 2 molecules of free hydroxylamine are added, as in the method described in the previous experiment. A white, crystalline substance is thus obtained which in form differs from that previously described. The crystals are much more dense, and may be recrystallized from methyl alcohol without change of composition, as is shown by analysis II. below. They are soluble in ethyl and methyl alcohol, and appear to be the most stable of any of the mercury compounds here described, yet upon warming considerable decomposition takes place. They are unstable in the presence of alkalies, either in a solution of water or alcohol.

   I. 0.3132 gram substance gave 0.1336 gram Hg.
       0.2372 gram substance gave 0.2843 gram AgCl.
       0.3410 gram substance gave 36.2 cc. N at 16° and 731.2
         mm. (corr.).
  II. 0.1456 gram substance gave 0.0615 gram Hg.
       0.2224 gram substance gave 0.2669 gram AgCl.

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.	Found.	
		I. Crude.	II. Recrystallized.
Hg	42.12	42.67	42.28
Cl	29.83	29.64	29.68
N	11.77	12.16	....

$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.—One molecule of mercuric chloride and 1 molecule of hydroxylamine hydrochloride are dissolved in methyl alcohol, cooled to —10°, and 3 molecules of free hydroxylamine contained in a concentrated solution of cold methyl or ethyl alcohol are slowly added with constant shaking. The solution remains clear for a few minutes, but when left standing for half an hour in brine and ice a considerable quantity of white crystals, which under the microscope appear uniform, separates. This salt is soluble in methyl and ethyl alcohol. Water also dissolves it completely, but the solution becomes turbid on standing a few minutes.

   I. 0.2284 gram substance gave 0.1043 gram Hg.
       0.2094 gram substance gave 0.2036 gram AgCl.
       0.2610 gram substance gave 29.4 cc. N at 20° and 728
         mm. (corr.).
  II. 0.2365 gram substance gave 0.1078 gram Hg.
       0.2802 gram substance gave 0.2751 gram AgCl.
       0.4692 gram substance gave 49.8 cc. N at 19° and 741
         mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.	Found.	
		I. From methyl alcohol.	II. From ethyl alcohol.
Hg	45.50	45.68	45.58
Cl	24.23	23.96	24.28
N	12.74	12.66	12.24

An attempt to recrystallize this substance from alcohol

shows that on warming there is considerable reduction into mercurous chloride, and when the solution is filtered and cooled, long, white crystals are obtained which, when analyzed, prove to be $HgCl_2(NH_2OH)_2$.

In analyzing the compound

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl,$$
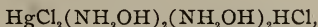
approximately one-half of the nitrogen is driven off at a low temperature, while to expel the remainder it is necessary to elevate the temperature very considerably, which indicates that the nitrogen is held bound in two different combinations which are expressed by the double-salt formula given above.

Other double salts of this nature were obtained, but when an attempt was made to purify them they decomposed completely or changed into the more stable forms before they could be separated.

Double Chloride of Mercury and Hydroxylamine,
$HgCl_2(NH_2OH)HCl$. — Hydroxylamine hydrochloride increases the solubility of mercuric chloride in alcohol or water, and a double salt is prepared by mixing hydroxylamine hydrochloride and mercuric chloride in the proportion of 1 molecule of each dissolved in as small an amount of water as possible. The solution is then placed over calcium chloride. In a few days white crystals of a double salt,

$$HgCl_2.(NH_2OH)HCl,$$

separate. The salt thus obtained is filtered by suction and dried on blotting-paper. Owing to its extreme solubility in both alcohol and water, it is difficult to purify. It is less soluble in ether, but when the solution is evaporated it separates as an oil and not as crystals. A sample left exposed to the air absorbed water and liquefied in an hour.

0.4585 gram substance gave 0.2710 gram Hg.

0.3712 gram substance gave 0.4719 gram AgCl.

0.7132 gram substance gave 24.3 cc. N at 17° and 738 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)HCl$.	Found.
Hg	58.73	59.10
Cl	31.25	31.98
N	4.11	3.94

When mercuric chloride is added to hydroxylamine hydrochloride in excess of the proportion of 1 : 1, and the solution is evaporated, mercuric chloride separates from the hydroxylamine ; and when in a proportion of less than 1 : 1, hydroxylamine hydrochloride separates free from mercury. If other salts are formed they dissociate upon concentration and cannot be obtained in this way. Hydroxylamine hydrochloride is almost insoluble in absolute ether. An attempt was made to prepare double salts by using ether as a solvent for mercuric chloride and adding powdered hydroxylamine hydrochloride to the solution in various proportions, but without success, for when 2.2 grams of hydroxylamine hydrochloride are added to 4.4 grams of mercuric chloride dissolved in 300 cc. of absolute ether, only 0.32 gram of hydroxylamine hydrochloride is dissolved after shaking the mixture for three days. When a small quantity of alcohol is present the solubility of the hydroxylamine hydrochloride is greatly increased, and when ligroin is added a voluminous white precipitate is produced. Analysis shows this to be a mixture which proved so unstable that no definite pure salt could be obtained.

$2HgCl_2.5(NH_2OH)_2HCl$.—This appears to be the most easily prepared of any of the mercury and hydroxylamine compounds here described. Apparently, whenever mercuric chloride is present in solution with excess of hydroxylamine hydrochloride and free hydroxylamine, this salt is formed. The compound, besides occurring as a by-product in several other experiments, is prepared in the following ways :

1. There is added to freshly prepared mercuric oxide, suspended in ethyl alcohol, a solution of hydroxylamine hydrochloride in ethyl alcohol. Both liquids are cooled down to —10° in brine and ice, mixed while cold, shaken thoroughly, and decanted from the undissolved mercuric oxide. The clear solution, on standing a few minutes, deposits flat, hexagonal crystals which must be immediately separated from the solution containing undissolved mercuric oxide. If they are left in contact with the oxide, reduction begins at once and spreads rapidly through all the crystals, leaving, finally, metallic mercury. By keeping the temperature below zero

this decomposition is retarded, but not wholly prevented. The crystals thus obtained are further purified by recrystallization from absolute alcohol (see Analysis I.).

2. A solution of hydroxylamine hydrochloride in methyl alcohol is added to mercuric oxide suspended in methyl alcohol. Crystals separate, similar in appearance to those separating from ethyl alcohol. The salt is more soluble in methyl alcohol than in ethyl alcohol, and decomposes more easily in the presence of the former. For the composition of these crystals see analysis II.

3. Two parts of free hydroxylamine are added to a mixture, in alcohol, of 1 part of mercuric chloride with 6 of hydroxylamine hydrochloride; by keeping all the solutions below zero, crystals similar to those previously described separate. They are purified by recrystallization. It will be seen that this method is similar to that used by Hofmann[1] for preparing his mercuramines (analysis III.).

4. The alcoholic filtrate from which the first crop of crystals separates contains in solution a considerable quantity of the same salt which may be precipitated by adding ether. The crystals thus formed are similar to those previously obtained (analysis IV.).

5. This same salt of mercury is obtained by adding a solution of hydroxylamine hydrochloride in water to mercuric oxide; but on account of the solubility of the salt, as well as its instability in water, this method is less satisfactory than those previously described.

    I. 0.4425 gram substance gave 0.1680 gram Hg.
       0.4752 gram substance gave 0.5860 gram AgCl.
       0.4860 gram substance gave 55 cc. N at 20° and 737 mm. (corr.).

    II. 0.5078 gram substance gave 0.1931 gram Hg.
       0.3883 gram substance gave 0.4771 gram AgCl.
       0.3246 gram substance gave 38 cc. N at 19° and 740.1 mm. (corr.).

    III. 0.2488 gram substance gave 0.0938 gram Hg.
       0.2085 gram substance gave 0.2587 gram AgCl.

[1] *Loc. cit.*

0.2385 gram substance gave 28.1 cc. N at 21°.5 and
733 mm. (corr.).

IV. 0.1718 gram substance gave 0.0651 gram Hg.
0.2129 gram AgCl.

	Calculated for $2HgCl_2.5(NH_2OH)_2HCl$.	I.	II.	III.	IV.
			Found.		
Hg	37.95	37.96	38.02	37.72	37.88
Cl	30.26	30.28	30.38	30.48	30.29
N	13.28	12.48	13.17	13.28	....

The salt is soluble in water at the ordinary temperature
with gradual reduction to mercurous chloride. When ammo-
nium hydroxide is added to a water solution, a white precipi-
tate is formed which turns black gradually in the cold, and
rapidly when heated. It is soluble in alcohol and ether; in
the presence of mercuric oxide it decomposes slowly at —10°,
and rapidly at higher temperatures. It is soluble in hydro-
chloric acid. The slightest trace of alkali causes decomposi-
tion.

Some experiments were carried out with mercurous chlo-
ride and hydroxylamine to determine whether a reaction takes
place between them, but owing to the insolubility of the mer-
curous chloride no definite results were obtained. Freshly
precipitated mercurous chloride, when treated with a solution
of hydroxylamine hydrochloride, was found to be slightly sol-
uble in it, but no combination of the two was observed. Mer-
curous chloride, when boiled with free hydroxylamine in
methyl alcohol in a flask fitted with a return condenser, was
reduced gradually to metallic mercury. In the cold the re-
duction takes place very slowly.

Mercuric Bromide and Hydroxylamine.—When mercuric
oxide is treated with a solution of normal hydroxylamine hy-
drobromide in an alcoholic solution cooled below zero, it dis-
solves, and if the solution is kept cool there separate white,
well-formed crystals of dihydroxylamine hydrobromide. The
solution contains mercuric bromide, which can be separated.
The reaction is probably represented by the following equa-
tion:

$$HgO + 4NH_2OH.HBr = HgBr_2 + 2(NH_2OH)_2HBr + H_2O.$$
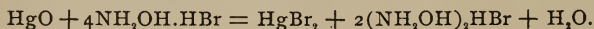
This is in marked contrast with the action of hydroxylamine hydrochloride on mercuric oxide.

$HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.—This compound is made by mixing mercuric bromide and normal hydroxylamine hydrobromide in the proper molecular proportions in methyl alcohol, cooling the mixture below zero, and adding to it, drop by drop, a solution of free hydroxylamine in methyl alcohol. On the addition of ether a white precipitate is formed, which is filtered and washed thoroughly with ether, care being taken to keep the salt cold. Analysis shows it to be $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$. It crystallizes in microscopic, quadratic plates. It is soluble in methyl alcohol with slow decomposition. The water solution becomes cloudy on standing a few minutes, indicating a reduction to mercurous bromide. It is readily decomposed by alkalies and is less stable than the corresponding chloride.

0.3911 gram substance gave 0.1189 gram Hg.

0.2879 gram substance gave 0.3326 gram AgBr.

0.1838 gram substance gave 14.4 cc. at 28° and 726.2 mm. (corr.).

	Calculated for $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.	Found.
Hg	30.58	30.42
Br	48.93	49.16
N	8.56	8.84

Methods similar to those by which $HgCl_2(NH_2OH)_2$ was obtained were tried to prepare the corresponding bromide, but without success.

Mercuric Iodide and Hydroxylamine.—When mercuric oxide was treated with hydroxylamine hydriodide the reduction to metallic mercury was so rapid, even in the cold, that no intermediate products could be separated.

Mercuric iodide was dissolved in alcohol and cooled below zero; to this solution hydroxylamine hydriodide was added. Yellow crystals of pure mercurous iodide soon separated. Attempts were made to precipitate some salt from the solution with ether and ligroin before the mercurous iodide separated, but without success. When these results are compared with

those obtained with the hydroxylamine hydrochloride and hydrobromide, an increase in reducing power from the hydrochloride to the hydriodide is noted.

Cadmium Bromide and Hydroxylamine.—Hydroxylamine combines with neither mercuric iodide nor bromide to form stable salts of the general formula $MX_2(NH_2OH)_2$. Attention was turned, therefore, toward cadmium, since its salts are in some respects similar to mercury, yet less easily reducible. Cadmium bromide was dissolved in alcohol, and to the solution free hydroxylamine was added. There was immediately formed a fine, white, crystalline precipitate of $CdBr_2(NH_2OH)_2$. This salt dissolves in hot water, forming in a few minutes a white, basic salt. It is readily soluble in dilute acids, insoluble in alcohol and ether.

0.2316 gram substance gave 0.1418 gram $CdSO_4$.

0.3965 gram substance gave 0.4404 gram AgBr.

0.0546 gram substance gave, on titration, 0.0105 gram NH_2OH.

0.3252 gram substance gave 24.6 cc. N at 27° and 721 mm. (corr.).

	Calculated for $CdBr_2(NH_2OH)_2$.	Found.
Cd	33.13	32.94
Br	47.33	47.26
NH_2OH	19.52	19.22
N	8.28	8.13

Cadmium Iodide and Hydroxylamine, $CdI_2(NH_2OH)_3$.— Pure hydroxylamine is added to a strong solution of cadmium iodide in alcohol. A precipitate, which dissolves readily, is formed when the addition is first made; but on allowing the solution to stand there separate large, colorless, acicular crystals of $CdI_2(NH_2OH)_3$.

0.2886 gram substance gave 0.1284 gram $CdSO_4$.

0.4155 gram substance gave 0.4185 gram AgI.

0.0916 gram substance gave, on titration, 0.0197 gram NH_2OH.

0.2456 gram substance gave 20.4 cc. N at 26° and 722 mm. (corr.).

	Calculated for CdI$_2$(NH$_2$OH)$_3$.	Found.
Cd	24.08	23.96
I	54.57	54.44
NH$_2$OH	21.29	21.52
N	9.03	9.08

This compound is stable, soluble in both alcohol and water, and insoluble in ether. Its formula emphasizes the tendency of iodine, already noted by Dunstan and Golding,[1] to combine with 3 molecules of hydroxylamine.

Analytical Methods.

The mercury in the preceding experiments was determined by dissolving the compounds in potassium cyanide, passing an electric current of 0.1 ampère and 2.5 volts for fourteen hours through the solution and weighing the metallic mercury.

For estimating the chlorine in those salts which are soluble without decomposition in water, the solution was slightly acidified with nitric acid and the mercury removed by means of hydrogen sulphide. By keeping it in a warm place for a few hours most of the hydrogen sulphide is driven off ; silver nitrate added to the solution made alkaline with ammonia removes the remainder ; then, on making the solution acid, the silver chloride is precipitated and determined in the usual manner. Though this method might have given good results with those chlorides which are insoluble or give precipitates in water, it was considered safer to heat them in a tube with calcium oxide, drive off the mercury, and determine the chlorine in the residue.

In the analysis of those salts containing sulphuric acid, a weighed quantity of the substance was fused with sodium carbonate and potassium nitrate to remove the mercury, and the residue treated with water and barium chloride in the usual manner.

I wish here to express my thanks to Dr. Felix Lengfeld, at whose suggestion and under whose careful help and guidance this work was carried out.

[1] *Loc. cit.*

ELECTRO-AFFINITY AS A BASIS FOR THE SYSTEMATIZATION OF INORGANIC COMPOUNDS.

By R. Abegg and G. Bodländer.

In connection with the attack upon our theory which Locke[1] has recently published, we might perhaps content ourselves with the general reflection that in the domain of chemistry hardly any valuable theory exists which does not have its weak points, and yet such theories are not on this account rejected and characterized as false, or, what is much more important, as useless. The periodic classification of the elements offers, perhaps, the best illustration. No one doubts its significance, in spite of the fact that several elements either do not show at all the analogies which the system requires or show them only to a very limited extent. We will, however, take up somewhat more in detail the various objections raised in the article referred to, as it is a matter of consequence to us that our ideas be not in an unjust way misunderstood in America, where research in inorganic chemistry, from the physico-chemical point of view, is making such gratifying progress.

The facts from which we started and to which we referred at the beginning of our article were as follows: The compounds whose constituents are easily separated by electrolysis from their solutions, that is, by the application of a small potential-difference, give solutions which contain comparatively small amounts of these constituents in the form of ions. The small ionic concentration, even of saturated solutions of these compounds, may be shown either in a slight solubility, or, when the solubility is large, in a slight dissociation, or in the transformation into a complex compound. Thus, the degree of solubility and the tendency to form undissociated or complex compounds depend, to a certain extent, upon the sum of the decomposition-potentials of the constituents. The greater this is, the greater is the solubility of the salt and the smaller its tendency to enter into complex compounds.

[1] This Journal, **27**, 105 (1902).

Nernst[1] has already pointed out that a limit for the solubility of a compound is set by the decomposition-potentials of its constituents. He shows that silver iodide could not form concentrated solutions since, on account of the small decomposition-potential of the iodine and the negative decomposition-potential of the silver, such solutions of it would of themselves decompose into silver and iodine. In fact, a calculation of the maximum solubilities which the three silver halides could have without being unstable, gives the following values expressed in mols per liter :

AgI.	AgBr.	AgCl.
0.007	82	37000

The actual solubilities are much smaller. However the order of the actual solubilities is the same as that of the limiting values ; and the distance from these limiting values affords a measure of the stability of the three compounds. The same fact is observed when one compares the order of the actual solubilities of the iodides of the nobler metals with the order of the calculated limiting values. In general, the ionic concentrations which are actually reached show the same sequence as the limiting values. The greater, however, the difference between the two values becomes, the greater becomes the field for the influence of other causes ; and the higher the solution-tension of the ions, the more do the limiting solubilities exceed their actual solubilities. Hence, from other causes, the solubilities may increase continually without materially diminishing the stability of the compound.

If the solubilities should continue to increase with the increase of the decomposition-potential of the constituents in the same ratio as in passing from silver chloride to thallium chloride, then the halides of the alkali metals would be salts of extreme solubility ; thus, the solubility of potassium chloride would be something like 10^{60} mols per liter. Such salts would, in dissolving, set free large amounts of energy, and therefore, in the solid form, would possess a large content of free energy. In consequence of this, such salts in the solid state would form modifications which are no longer directly comparable with those of the less soluble salts.

[1] Ber. d. chem. Ges., **30**, 1547 (1897).

Hence the solubility of a salt is by no means dependent solely upon the solvent and the chemical character of the salt in the dissolved state, but it depends also upon the solid modification with which the solution is in equilibrium. And one may assume that the same self-preserving law which hinders a great solubility of silver iodide, also operates to give solid potassium chloride a form less soluble than that which would be directly comparable with thallium chloride or silver chloride. In our paper we cited illustrations and called explicit attention to inversions in the order of solubilities which are ascribable to this cause. We may designate, in such cases, the solubility diminishing with increasing decomposition-potential as "inverse solubility."

The views put forward by Richards[1] give excellent evidence in favor of our suggestions concerning inverse solubilities. He states, namely, that the volumes of the chlorides of the heavy metals from zinc to silver exceed those of the corresponding metals by about 17 units, while the excess in volume in the case of magnesium is 15, of sodium only 4.2, and in the cases of potassium and rubidium it is even negative. This proves that in the latter cases there is an abnormally great contraction or association of the salt molecules corresponding to an increased energy of formation E_s in the solubility-formula of Bodländer,[2]

$$0.116 \log p = E_a + E_k - E_s,$$

where an increase of E_s obviously lowers the solubility p.

In the same sense, we find the order of the differences (Δ) between the equivalent volumes of the chlorides of the following metals and between those of the potassium salts of the halogens (see Richards' tables: *loc. cit.*, pp. 599, 602, 609) to be apparently in complete agreement with the inverse solubilities as found in these series. The values of Δ are, namely, as follows:

Chlorides :	Mg	Ca	Sr	Ba	Li	Na	K
	15.3	12.3	8.7	8.4	9.0	3.5	—7.7

Potassium salts :	J	Br	Cl
	28.1	18.7	12.5

[1] Ztschr. phys. Chem., **40**, 183, 597.
[2] *Ibid.*, **27**, 55; Ztschr. anorg. Chem., **20**, 460.

Besides this, the other influences which may affect the solubility of compounds of strong ions, such as the formation of hydrates and of inner complexes, are various and may operate partially in opposition to each other, so that a simple general law in the case of easily soluble compounds is not to be expected, nor did we make the assumption that such existed. We pointed out only certain regularities.

Although weak ions cannot form easily soluble salts, it is not impossible for salts formed from strong ions to be difficultly soluble. The law of self-preservation prevents the former case, but the latter fact is not inconsistent with the validity of the law. Thus, it is so self-evident that the small solubility of calcium fluoride or barium sulphate cannot be attributed to the small discharging potential of its ions that it was scarcely necessary to emphasize,—what, however, we did not neglect to call attention to,—that here influences other than the electro-affinity must come into play. When the small electro-affinity of the constituents of a salt give it a low solubility, then this small electro-affinity also causes the same substances to easily become constituents of complex salts. Thus, Locke has completely misunderstood us when he assumes that, according to our views, all substances which form insoluble compounds must also form complex compounds. This is really the case only when small electro-affinity is responsible for the insolubility of the compound. A tendency of an ion to form both slightly soluble salts and complex compounds is a proof of small electro-affinity; but, as might be expected, the electro-affinity is large where the former tendency, but not the latter one, is very marked, as in the case of the alkaline-earth metals. When the difficultly soluble substance becomes easily a constituent of a complex ion, we may perhaps consider it a direct evidence that the low solubility of the compound is due to small electro-affinity, although experimental data are here lacking.

Of course, the objection may now be raised, that one may interpret each individual case with the aid of such additional hypotheses, and we by no means hesitate to say that it is a matter of personal preference whether such additional as-

sumptions be accepted, and that the satisfactory application of them to individual cases belongs essentially to the future.

In our opinion, there is at present no single case irreconcilable with our theory, since the possible explanations for the apparent exceptions have not yet been investigated. We therefore consider our conception solely as a basis of investigation, and have published it since the application to single cases is far beyond the working ability of two men, and a general participation in the solution of inorganic problems appeared to us desirable.

We must further state in reference to the solubilities quoted by Locke that the table on page 111 contains in many places striking errors unfavorable to us. For example, zinc chromate is known only as a component of an isomorphous mixture, so that its own solubility is unknown. Barium hypophosphite, according to Wurtz,[1] is soluble in 3.5 parts of water, hence, not insoluble. Barium iodate is soluble in 3018 parts of water, zinc iodate in 114 parts,— a difference which does not justify the assertion that the former is insoluble and the latter soluble.

According to Rose,[2] zinc phosphite is more difficultly soluble than magnesium phosphite. The latter is given as difficultly soluble ; nevertheless zinc sulphate causes a precipitate in its solution, so that zinc phosphite must be still less soluble. Zinc sulphite is slightly soluble, probably less so than barium sulphite. Zinc oxalate is at least as insoluble as barium oxalate, but it is of importance to note that it easily forms complex salts, which one of us is at present engaged in investigating. Barium cyanide, if free from water, dissolves, according to Joannis,[3] in 1.25 parts of water, and is extremely hygroscopic. The hydrate, with 2 molecules of water, is deliquescent.

In respect to the alums and the double salts of the type of $K_2Mg(SO_4)_2.6H_2O$, the same statements apply as in the case of the simple soluble salts. We must further take into account the fact that the solubility of such double salts, owing to

[1] Ann. chim. phys., [3], **7**, 35.
[2] Pogg. Ann., **9**, 29.
[3] Ann. chim. phys., [5], **26**, 493.

complex dissociation, the Nernst-effect (decrease of solubility by salts having a common ion), and hydrate formation in the solution, is quite a complicated phenomenon, to which it is scarcely to be expected that simple laws will apply, especially when one does not know the single factors.

In reference to the ammonia complexes of magnesium (p. 113) we may refer Locke to the work of Gaus,[1] by which their existence is proved and discussed in accordance with our theory.

The presence in a solution of salts having a common ion is the reason why thallium chloride is less soluble in chloride solutions than in water, as was long ago explained by the Nernst theory and experimentally investigated by A. A. Noyes.[2] The increase of solubility due to the formation of complexes can be expected only in the case of very great concentration of the chlorine ions ; in the case of silver, a nobler metal, and hence more inclined to form complexes, this increase is only noticeable with large concentrations of the chlorine ions. This is an exact confirmation of the rule, and not a departure from it.

In regard to the complex ammonia compounds, the formulas and degrees of stability of the dissolved ions, which alone are to be considered, are still too little known. The method of Dawson and McCrae does not suffice to give information about the stability of the complexes. Besides, we must also consider that here, as in other cases, in addition to the predominating influence of electro-affinity, the individual atomic affinities come into play, in this case between the metal and ammonia.

The formation of a complex ammonia compound is only possible in the presence of an excess of free ammonia. But this gives hydroxyl ions, and whether this ammonia complex is capable of existing in detectable amounts depends not only upon its greater or less stability, but also upon the greater or less stability of the hydroxide. The stable solid compounds of ferric chloride and aluminium chloride[3] with ammonia de-

[1] Ztschr. anorg. Chem., **23,** 157 (1900).

[2] Ztschr. phys. Chem., **6,** 249 (1890).

[3] Dammer : Handbuch., III., 94, 311.

compose largely in water, while the cobalt-ammonia compound remains intact. This need not be attributed to the fact that fewer free cobalt ions and ammonia molecules exist in the presence of the cobalt-ammonia ion than with the iron-ammonia ion, but may be explained by saying that fewer ferric ions than cobaltic ions can exist in the presence of the hydroxyl ions which are formed by the ammonia. This illustrates the fact that electro-affinity which influences the solubility of the hydroxide, as well as the stability of the ammonia complex, may cause two opposite effects whose resultant cannot be foretold without further investigation. The small solubility of the basic salts in comparison with the neutral salts may be due to the fact that these dissociate according to the general formula $(M^{II}Cl)\cdot(OH)$. Here the electro-affinity leads us to expect that the basic salt be more easily soluble than the hydroxide, which agrees with the facts. The inverse solubility of the alkali salts (115) is, in our opinion, in harmony with the views given above.

In general, it appears as if it were on account of hydration that the very soluble salts deviate most from the fundamental solubility principle of our theory, and it is true that, according to the law of mass-action, the higher the concentration of the constituents which can be hydrated the greater the hydration will be.

On the other hand, the research on solubilities of difficultly soluble substances carried out by Cl. Immerwahr[1] shows a good agreement with our theory. Locke emphasizes especially, and in great detail, that the solubilities of the double salts of the type $K_2Mg(SO_4)_2.6H_2O$, of the alums, and of the double halides of caesium do not correspond with the demands of our ideas. These salts are present in solution only partially as complexes[2] and partially in the form of the single salts, and we have scarcely any information concerning their quantitative relations. Both components influence mutually the dissociation, and thus, to a great extent, the solubility, so that the total solubility of such a double salt affords no information concerning the concentration and stability of the complex ion.

[1] Ztschr. f. Elektrochemie, **7**, 477.
[2] See Rieger: *Ibid.*, **7**, 863, 871 (1901).

The homologous series of the alkali-chromium alums affords an evident numerical series of the solubility, but this is hardly to be considered as an objection against the presence of secondary solubility influences, for in homologous series regular gradations which underlie these secondary influences might lead to such results.

The series of objections with which Locke closes his paper seem expressly calculated to reproach us with being obscure. He avoids, however, a concrete discussion, which might be more in our favor. Thus, as a matter of fact, the iodates and periodates of metals, whose iodides are typically difficultly soluble, are more soluble than the iodides. Locke evidently expects that every reader will recall the much better known alkali compounds where the inverse solubility conditions occur, which were discussed above and in our previous article.

The greater solubility of the mercuric salts, as compared with mercurous salts, was also considered in our original paper (pp. 466–467).

The behavior of these salts completely agrees with our views, considering only their ionic concentrations, to which the theory solely applies, but by no means to the total solubility, for it is not at all improbable that the concentration of mercurous ions in a saturated solution of calomel is greater than the concentration of the mercuric ions in a saturated solution of the sublimate. The mercuric salts form complex salts easily, mercurous salts almost not at all. This agrees perfectly with the position of the metals in the order of their electrolytical potentials, since it has been shown by Ogg[1] and Abel[2] that mercuric mercury is actually more noble than mercurous mercury.

However, we do not wish to put forward our ideas as a dogma, nor to urge prematurely on the chemical world their general acceptance, but we present them as a working hypothesis, the value of which is to be measured by its fruits. We may further justify the presentation of our theory by

[1] Ogg : Ztschr. phys. Chem., **27**, 285 (1898).
[2] Abel : Ztschr. anorg. Chem., **26**, 361 (1901).

quoting from a recent paper by Richards,[1] who says: "No hypothesis has as yet been proposed which has been found completely satisfactory; our knowledge is incommensurable for all existing possibilities. However, when one finds that a certain theory explains some relations better than other hypotheses, it may serve to suggest new experimental investigations. Such a service is of course the best that an hypothesis is able to accomplish."

Inorganic chemistry requires especially for its development along physico-chemical lines broad generalizations, and we have introduced the idea of electro-affinity in the hope that it may prove to be of this character. By reason of the lack of a comprehensive theory the large domain of complex compounds is less inviting than it should be.

If, by our views, any new investigators are led to this field, which actually has been the case to some extent already, we shall consider that alone as a successful outcome, even if, in contrast to the results thus far obtained, further investigations should show that the directing effect of electro-affinity is made unrecognizable by the secondary influences present.

What Locke published against our theory, so far as it is not directly wrong, has to do with influences, which, like the partial splitting of double salts, had been known for some time, and had already been taken into consideration by ourselves. It does not, by any means, decide the question of the usefulness of our theory.

BRESLAU AND BRAUNSCHWEIG, May, 1902.

XXI.—CAMPHORIC ACID.

[TWELFTH PAPER.]

SYNTHESIS OF TRIMETHYLPARACONIC ACID.

BY WILLIAM A. NOYES AND AUSTIN M. PATTERSON.

The experiments here described were undertaken for the purpose of effecting a synthesis of the camphoric acid corre-

[1] *Ztschr. phys. Chem.*, **40**, 183, 184 (1902). The conclusions which Richards draws from the consideration of the atomic volume, about the affinity between like atoms of an element offer, perhaps, a way to get from the experimentally determined electrolytical potential to what is more important for our theory, the real electro-affinity.

sponding to Bredt's formula for camphor. The synthesis is not completed, but enough progress has been made to make it seem desirable to publish our results.

Some years ago, Fittig and Jayne[1] showed that benzoic aldehyde and sodium succinate condense, when heated with acetic anhydride, giving phenylparaconic acid,

$$
\begin{array}{c}
CH_2{-}CO \\
| \qquad\qquad {\Large >}O \\
CH{-}CH{-}C_6H_5. \\
| \\
CO_2H
\end{array}
$$
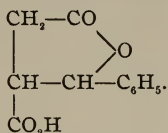
Later, Fittig and his students applied the reaction to include several other aldehydes, and also to include methylsuccinic acid.

So far as we are aware, no attempt has ever been made to use formic aldehyde for this reaction. We have succeeded in doing this and have effected a remarkably clean synthesis of trimethylparaconic acid,

$$
\begin{array}{c}
CH_3 \\
\qquad {\Large >}C{-}CO \\
CH_3 \qquad | \qquad\qquad {\Large >}O, \\
CH_3{-}C{-}CH_2 \\
| \\
CO_2H
\end{array}
$$

as follows :
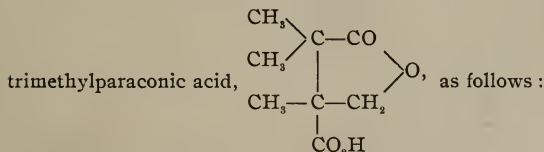
Trioxymethylene was prepared by evaporating a 40 per cent solution of formic aldehyde to about one-half its volume on the water-bath and drying the residue in a vacuum desiccator. About 12 grams of the dry trioxymethylene were obtained from 50 cc. of the solution. This still retains 7 to 9 per cent of water.[2] Thirteen and two-tenths grams of the sodium salt of trimethylsuccinic acid, 3.5 grams of trioxymethylene, and 9.9 grams of acetic anhydride were heated in a sealed tube at 120° to 140° for two days. The duration of the heating was probably excessive, but no experiments have been made to determine the minimum time which is allowable for the reaction. There was a slight pressure in the tube when opened. The contents dissolved easily in hot water.

[1] Ann. Chem. (Liebig), **216**, 97.
[2] Ann. chim. phys., [7], **15**, 551.

The solution was distilled with steam to remove formic aldehyde, then concentrated, acidified with hydrochloric acid, and extracted three times with ether. The residue left on distilling the ether was heated on the water-bath for some time under diminished pressure to remove acetic acid and acetic anhydride. A titration of a portion of this residue indicated that the conversion to trimethylparaconic acid was practically complete. 0.1562 gram required for neutralization 8.9 cc. of N/10 potassium hydroxide. Theory requires 9.1 cc., while the theory for trimethylsuccinic acid is 19.5 cc.

The *trimethylparaconic acid* was purified by crystallization from hot benzene, in which it is difficultly soluble. It may also be crystallized from dilute alcohol, which is a more suitable solvent for use with larger amounts. The pure acid melts with decomposition at 256° to 257°.

0.1965 gram substance gave 0.4015 gram CO_2 and 0.1209 gram H_2O.

	Calculated for $C_8H_{12}O_4$.	Found.
C	55.77	55.72
H	7.04	6.84

0.1609 gram required 9.26 cc. N/10 potassium hydroxide. Theory requires 9.35 cc.

When the acid is warmed with an excess of sodium hydroxide it is converted into the sodium salt of trimethylitamalic acid,

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C - CO_2Na$$
$$|$$
$$CH_3 - C - CH_2OH$$
$$|$$
$$CO_2Na$$
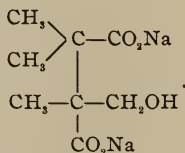
By heating in this manner on the water-bath for twenty hours, neutralizing the solution with nitric acid, and precipitating with a slight excess of a concentrated solution of silver nitrate, a nearly quantitative conversion to the silver salt can be effected. The salt is semi-crystalline in character and difficultly soluble. The salt was dried in a vacuum desicca-

tor which was heated to 45° to 50° to hasten the process. This salt gave 53.41 per cent of silver. Theory requires 53.46 per cent.

Diethyl Ester of Trimethylitamalic Acid,

$$\begin{array}{l} \mathrm{CH_3}\\ {>}\mathrm{C-CO_2C_2H_5}\\ \mathrm{CH_3}|\\ |\\ \mathrm{CH_3-C-CH_2OH}\\ |\\ \mathrm{CO_2C_2H_5} \end{array}$$
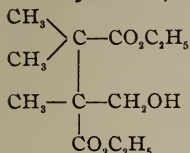
.—Twenty-three grams of the dry silver salt, 25 grams of dry ether, and 25 grams of ethyl iodide were brought together in a flask connected with an upright condenser. The reaction began spontaneously after five to ten minutes, and was continued by warming gently on the waterbath for an hour and a half. The product was filtered and the residue extracted with ether several times. Ten and seventenths grams of the ester were obtained, while the calculated amount is 14 grams. The ester is a viscous oil which did not solidify. An analysis of the ester from a second preparation in which less pure materials were used, was not satisfactory. We have not been able to repeat the preparation but the method used leaves little doubt of the composition of the product.

It was next desired to obtain the ethyl ester of bromtetra-methylsuccinic acid,

$$\begin{array}{l} \mathrm{CH_3}\\ {>}\mathrm{C-CO_2C_2H_5}\\ \mathrm{CH_3}|\\ |\\ \mathrm{CH_3}|\\ {>}\mathrm{C-CO_2C_2H_5}\\ \mathrm{CH_2Br} \end{array}$$
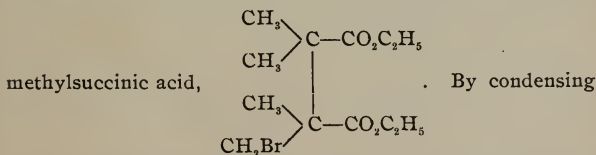
. By condensing this with malonic ester, saponifying the product, and splitting off carbon dioxide, it would seem possible to obtain homocam-phoronic acid,

$$\begin{array}{l} \mathrm{CH_3}\\ {>}\mathrm{C-CO_2H}\\ \mathrm{CH_3}|\\ |\\ \mathrm{CH_3-C-CO_2H}\\ |\\ \mathrm{CH_2-CH_2-CO_2H} \end{array}$$
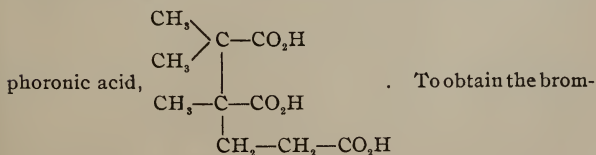
. To obtain the brom-

ester, 10.7 grams of the diethyl ester described above were dropped into 8 grams of phosphorus tribromide carefully cooled with a freezing-mixture. The mixture was allowed to stand for two or three hours and was poured on crushed ice. The ester was separated with ether and dried *in vacuo.* In spite of the precautions taken, ethyl bromide had been split off, the resultant ester contained only a trace of bromine, and on analysis it was found to be the

Ethyl Ester of Trimethylparaconic Acid,

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \diagup \end{array} C\!-\!CO \\ \quad\quad | \qquad\qquad \diagdown O.\!- \\ CH_3\!-\!\underset{|}{C}\!-\!CH_2 \\ \quad\;\; CO_2C_2H_5$$
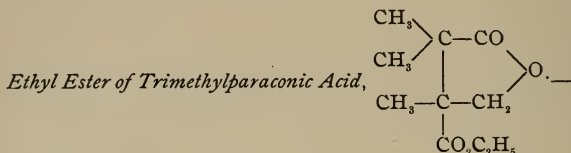
Analysis :

	Calculated for $C_{10}H_{16}O_4$.	Found.
C	60.00	59.23
H	8.00	8.24

The same ester was obtained by heating trimethylparaconic acid with alcohol and hydrochloric acid in a sealed tube, in the water-bath, for some hours. When prepared in this manner, it solidified on standing and then melted at 34°.5. The analysis gave : carbon, 59.81 ; hydrogen, 8.03. See above.

Whether it will be possible to overcome the difficulty encountered and obtain the ethyl ester of the bromtetramethylsuccinic acid in some other manner, it is impossible now to foresee. In any case, the work with the trimethylparaconic acid will be continued, and it is hoped that by means of it a synthesis of Bredt's camphoric acid can be effected.

TERRE HAUTE, IND.,
June 23, 1902.

THE ACTION OF LIGHT ON CINNAMYLIDENE-MALONIC ACID.

BY ELMER P. KOHLER.

While working with some yellow, unsaturated ketones prepared from cinnamic aldehyde I observed that they turned white when exposed to direct sunlight. The change is evidently of the same character as that observed by Liebermann[1] in the case of cinnamylidenemalonic acid, and as it seemed easier to follow such a change with an unsaturated acid than with an unsaturated ketone, I undertook a study of the acid obtained by Liebermann. The last number of the *Berichte*[2] contains an article by Riiber on the synthesis of α-truxillic acid, which, to some extent, deals with the same subject. I therefore publish the results obtained with cinnamylidene-malonic acid, reserving the work on cinnamylidene ketones for a later paper.

1. Method of Exposure.

Liebermann exposed the solid acid under a bell-jar to the direct rays of the sun and obtained almost complete transformation after two to three weeks. This method is too tedious for the preparation of larger quantities of material. The change is never complete and the product is hard to purify, as can be seen from the uncertain melting-points obtained by Liebermann. After trying a number of different conditions, I adopted the following method of procedure, which gives results that are quite satisfactory.

A solution of 20 grams of the acid, in the required amount of dilute sodium carbonate solution, is poured into an excess of dilute hydrochloric acid contained in a 3-liter balloon-flask and the liquid diluted to 2 liters. The acid is thus obtained as an impalpable yellow powder which remains suspended in the liquid for a long time. The powder changes rapidly when the flask is exposed to the direct rays of the sun, and if the flask is shaken about once an hour the change is complete

[1] Ber. d. chem. Ges., **28**, 1440.
[2] *Ibid.*, **35**, 2411.

after exposure of twenty to thirty hours to bright summer sunlight.

The product is separated by filtration, washed with boiling water, and dissolved, while still moist, in the minimum quantity of glacial acetic acid. On cooling this solution the substance separates in small, lustrous prisms. These are washed with acetic acid and ether and dried on the water-bath. Prepared in this way, the substance is pure white in color and melts sharply at 195°. It decomposes immediately after melting. It is readily soluble in alcohol and acetone, moderately soluble in glacial acetic acid, almost insoluble in ether, chloroform and ligroin. It crystallizes well only from glacial acetic acid.

The molecular weight, determined in acetone, showed that the substance is formed by the condensation of 2 molecules of cinnamylidenemalonic acid :

$$K = 1725.$$

Acetone. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
81.2690	1.2110	0.060	428
"	2.4320	0.128	403
"	3.3280	0.180	395
	Calculated for $(C_{12}H_{10}O_4)_2$,		436

The oxidation of the substance with potassium permanganate in alkaline solution gave essentially the same products as those obtained by Riiber. Twenty grams of the substance were dissolved in sodium carbonate solution. The resulting liquid was cooled with crushed ice and treated with 25 grams of potassium permanganate dissolved in ice-water. After standing over night in the ice-chest the oxides of manganese were removed by filtration and the filtrate acidified. The colorless acid which separated (4.9 grams) was recrystallized from methyl alcohol, from which it separated in large, colorless plates containing methyl alcohol of crystallization which was given off as soon as the crystals were removed from the mother-liquor. The substance melted at 274° and gave the following results on analysis :

I. 0.2206 gram substance gave 0.5904 gram CO_2 and 0.1080 gram H_2O.

II. 0.2004 gram substance gave 0.5353 gram CO_2 and 0.1010 gram H_2O.

	Calculated for $C_{18}H_{16}O_4$.	Found. I.	II.
C	72.97	72.98	72.88
H	5.40	5.60	5.44

The substance was identified as α-truxillic acid by its melting-point and the melting-points of the methyl and ethyl esters obtained by saturating its solution in the corresponding alcohols with hydrochloric acid. It crystallizes from cold methyl alcohol with 2 molecules of methyl alcohol of crystallization.

0.1220 gram substance lost 0.0198 gram at 100°.

	Calculated for $C_{18}H_{16}O_4.2CH_3OH$.	Found.
CH_3OH	16.00	16.20

The filtrate from the α-truxillic acid was extracted with ether which took up two substances : benzoic acid, identified as ethyl benzoate, and an oily acid that has not yet been obtained in pure condition.

The extracted liquid was neutralized with ammonia and treated with a solution of calcium chloride. The fine white precipitate which formed was found to be calcium oxalate.

The products of oxidation are, therefore, α-truxillic acid, benzoic acid, an oil of unknown structure, and oxalic acid. The formation of α-truxillic acid indicates that the substance contains a tetramethylene ring and leads to the formula of a diphenyltetramethylenebismethylenemalonic acid :

$$C_6H_5CH.CH.CH=C\begin{matrix}CO_2H\\CO_2H\end{matrix}$$
$$HO_2C\begin{matrix}\\\end{matrix}C=CH.CH.CHC_6H_5$$
$$HO_2C$$
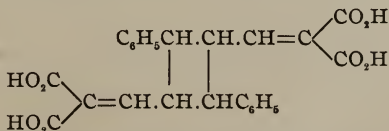
This formula agrees perfectly with the addition-reactions described below.

Since the change from cinnamylidenemalonic acid to a sub-

stance with this formula involves only the first set of double linkages, it seemed possible to transform some of the derivatives of the acid in the same way ; but this is not the case. The sodium salt, the acid potassium salt, the methyl and ethyl esters, and the amide were exposed to the light under a variety of conditions, but no change could be detected in any of them. All of these substances are colorless while the acid is yellow, and judging by the results obtained with cinnamenyl ketones only the colored compounds are affected by sunlight. The yellow cinnamenylacetone, for example, is very sensitive to light while cinnamenylacetic acid is not.

II. Addition-Reactions of Diphenyltetramethylenebismethylene-malonic Acid.

1. With Hydrochloric Acid.—The acid combines very readily with 2 molecules of hydrochloric acid. When a solution of the acid in methyl alcohol was saturated with hydrochloric acid the insoluble methyl ester of an acid, formed by the addition of 2 molecules of hydrochloric acid, crystallized out. The substance was washed with alcohol and recrystallized from acetone.

0.1895 gram substance gave 0.4120 gram CO_2 and 0.1022 gram H_2O.

	Calculated for $C_{28}H_{30}Cl_2O_8$.	Found.
C	59.46	59.30
H	5.31	5.38

The ester is almost insoluble in methyl alcohol, ethyl alcohol, chloroform, and ether. It is readily soluble in boiling acetone, from which it separates, on cooling, in thick needles. It melts at 197° to 198° with evolution of hydrochloric acid.

The corresponding ethyl ester was made by saturating a solution of the acid in absolute alcohol with hydrochloric acid and allowing the liquid to stand for several days. It begins to separate after a few hours, but the amount of the product increases for several days. The ethyl ester is somewhat more soluble in boiling alcohol than the methyl ester and was purified by recrystallization from absolute alcohol.

0.2835 gram substance gave 0.6404 gram CO_2 and 0.1548 gram H_2O.

	Calculated for $C_{30}H_{34}Cl_2O_8$.	Found.
C	61.83	61.82
H	6.11	6.07

The ester crystallizes from acetone or absolute alcohol in long, slender needles. It is only very slightly soluble in ether, chloroform, methyl alcohol, and cold absolute alcohol. It is moderately soluble in boiling alcohol, readily soluble in acetone. It melts with decomposition at 185°.

2. Addition of Bromine.—The acid readily combines with 2 molecules of bromine, but the resulting addition-product is exceedingly unstable. It easily loses carbon dioxide and hydrobromic acid, and passes into a bromine substitution-product of an unsaturated dibasic acid, diphenyltetramethylene-bisbrommethyleneacetic acid.

Bromine was added, drop by drop, to 10 grams (1 molecule) of the substance suspended in glacial acetic acid until the color of bromine was permanent. The bromine disappeared rapidly until 7.5 grams (2 molecules) had been added. The acid dissolved as it was brominated. There was no evolution of carbon dioxide and the liquid contained only a small quantity of hydrobromic acid. The process was, therefore, one of direct addition. From the solution crushed ice precipitated a colorless product in clear, lustrous plates. These, however, rapidly changed into an impalpable white powder, while carbon dioxide was evolved and hydrobromic acid went into solution. The powder was filtered off, washed with water, dissolved in absolute alcohol, and reprecipitated by pouring the hot solution into twice its volume of hot water. It separated in colorless plates, which melted with decomposition at 245°. An analysis gave the following results:

0.1599 gram substance gave 0.3073 gram CO_2 and 0.0533 gram H_2O.

	Calculated for $C_{22}H_{18}Br_2O_4$.	Found.
C	52.17	52.36
H	3.56	3.70

The acid is insoluble in chloroform and ligroin, slightly soluble in ether and benzene, readily soluble in alcohol and acetone. In alkaline solution potassium permanganate oxidizes it rapidly and quantitatively to α-truxillic acid. This is doubtless the easiest way of preparing α-truxillic acid. For this purpose the crude product obtained by exposing cinnamylidenemalonic acid to the sunlight is filtered off, the moist solid suspended in its own weight of glacial acetic acid, and bromine added until the color is permanent. The solution is then poured into ten times its volume of boiling water and the precipitate removed by filtration as soon as the temperature of the water has fallen to 80°. After washing with cold water the precipitate is dissolved in a slight excess of a saturated solution of sodium carbonate. To the solution obtained in this way a saturated solution of potassium permanganate is added, at the ordinary temperature, until the color of the permanganate remains after vigorous shaking. The oxides of manganese are then dissolved by adding an excess of sodium bisulphite and acidifying with dilute sulphuric acid or, better, by passing a current of sulphur dioxide through the liquid. In either case the α-truxillic acid separates out in small, colorless grains, which melt above 270°, and after one crystallization from methyl alcohol, at 274°. The changes are represented by the following equations :

I.

$$C_6H_5CHCHCH=C\begin{matrix}CO_2H\\CO_2H\end{matrix}$$
$$HO_2C\begin{matrix}\\\end{matrix}C=HCCHCHC_6H_5\qquad+\ 2Br_2\ =$$
$$HO_2C$$

$$C_6H_5CHCHCHBrCBr\begin{matrix}CO_2H\\CO_2H\end{matrix}$$
$$HO_2C\begin{matrix}\\\end{matrix}BrCBrHCCHCHC_6H_5\qquad\longrightarrow$$
$$HO_2C$$

$$C_6H_5CHCHCBr=CHCO_2H$$
$$HO_2CHCBrCCHCHC_6H_5\qquad+\ 2HBr\ +\ 2CO_2\ ;$$

II.
$$C_6H_5CHCHCBr{=}CHCO_2H$$
$$HO_2CHC{=}BrCCHCHC_6H_5 + 6CO + 2H_2O =$$

$$C_6H_5CHCHCO_2H \qquad COOH$$
$$HO_2CCHCHC_6H_5 + 2HBr + 2 \Big|$$
$$COOH$$
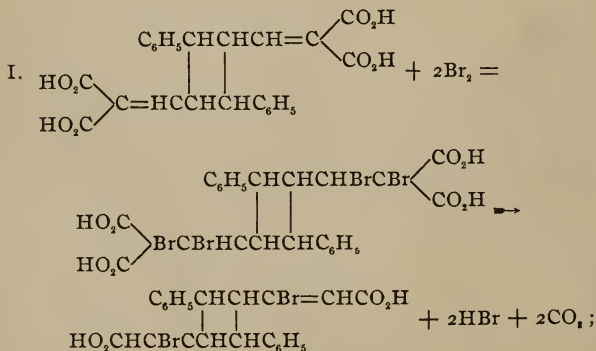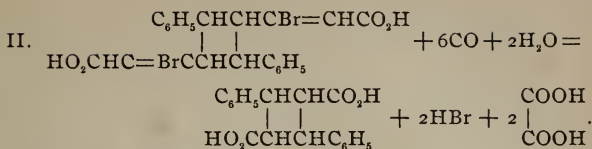
All of these reactions, beginning with cinnamylidenemalonic acid, are quantitative.

The methyl ester of diphenyltetramethylenebisbrommethyleneacetic acid was made by saturating a solution of the acid in methyl alcohol with hydrochloric acid and separating the product in the usual way. After recrystallization from alcohol the ester melted at 115°.

0.2050 gram substance gave 0.4043 gram CO_2 and 0.0780 gram H_2O.

	Calculated for $C_{24}H_{22}Br_2O_4$.	Found.
C	53·93	53·74
H	4·12	4·31

The ester is moderately soluble in methyl alcohol, readily soluble in ordinary alcohol and in acetone.

3. Addition of Acid Potassium Sulphite.—The acid combines with acid sulphites in the cold. A saturated solution of potassium sulphite was added to 5 grams of the acid until a clear solution resulted. After standing for eight hours an excess of dilute hydrochloric acid was added to the solution. An acid salt separated in fine, white needles. After one recrystallization from boiling water the air-dried salt was analyzed with the following results:

 I. 0.1000 gram substance lost 0.0176 gram at 110°.
 II. 0.1959 gram substance gave 0.0410 gram K_2SO_4.
 III. 0.1639 gram substance gave 0.0349 gram K_2SO_4.

	Calculated for $C_{24}H_{22}O_{14}S_2K_2.6H_2O$.	I.	Found. II.	III.
H_2O	17.56	17.6	....	....
K	9.51	....	9.37	9.53

The salt is moderately soluble in cold water, readily soluble in boiling water, insoluble in alcohol. The corresponding neutral salt is very readily soluble in water.

III. Change of Diphenyltetramethylenebismethylenemalonic Acid into Cinnamylidenemalonic Acid.

As pointed out above, all the addition-reactions of the acid agree in composition and properties with the formula assigned to it, and it would be difficult to account for them by any other formula. The only fact that is not clearly accounted for by the formula is the surprising ease with which the acid can be changed back into cinnamylidenemalonic acid. The acid dissolves in cold concentrated sulphuric acid, and when the yellow solution is poured into ice-water pure cinnamylidene-malonic acid is precipitated. It is known that the tetra-methylene ring is easily opened, and Liebermann[1] found that α-truxillic acid changes into cinnamic acid on distillation, but nothing that is known about tetramethylene compounds could lead to the expectation that the ring would be completely broken down by simple solution in cold sulphuric acid. The change seems to be connected with the peculiar character of the side chain since none of the other substances described in this paper is affected in the least by solution in concentrated sulphuric acid.

BRYN MAWR COLLEGE,
CHEMICAL LABORATORY,
    July, 1902.

NOTE.

The Detection of Hydrocyanic Acid in the Presence of Sulpho-cyanic, Hydroferrocyanic, and Hydroferricyanic Acids and Their Salts.

Take about 25 to 50 cc. of the solution, from which the heavy metals and alkaline earths have been removed by boiling with sodium carbonate, add caustic potash and about 0.5 gram of pure aluminium filings. Let stand in a loosely stoppered flask about fifteen minutes. The potassium ferricyanide is reduced to ferrocyanide,

$$K_3Fe(CN)_6 + 4KOH + Al =$$
$$K_4Fe(CN)_6 + Al(OK)_3 + H_2O + H_2.$$
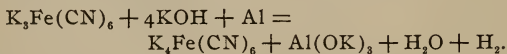
Decant off a small portion of the clear solution, acidify, and add ferrous sulphate to test whether all the ferricyanide has been

[1] Ber. d. chem. Ges., **22**, 124.

reduced. If the reduction is complete, acidify the entire solution with hydrochloric acid, and precipitate the hydroferrocyanic acid with an excess of mercuric chloride solution.

$$H_4Fe(CN)_6 + HgCl_2 = Hg_2Fe(CN)_6 + 4HCl.$$
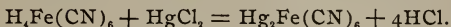
Shake well for a few minutes (do not heat), and then filter, repeating if necessary, until the filtrate is perfectly clear. Wash the precipitate with a little dilute mercuric chloride solution, and, if clear, add to the first filtrate. Now make alkaline with caustic potash, and filter off the mercuric oxide, wash, add to the filtrate a solution of ferrous sulphate and boil. The potassium cyanide is converted into potassium ferrocyanide:

$$FeSO_4 + 2KOH = Fe(OH)_2 + K_2SO_4 ;$$
$$Fe(OH)_2 + 2KCN = Fe(CN)_2 + 2KOH ;$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$
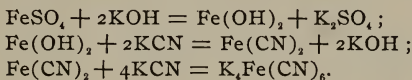
Filter and wash, adding the wash-water to the filtrate. Acidify with hydrochloric acid and add ferric chloride solution. A dirt-colored solution is obtained. The iron sulphocyanate formed is decolorized by mercuric chloride, and the precipitate of Prussian blue can then be seen. If the solution is quite acid, and only a small quantity of hydrocyanic acid was present originally, the solution is green and no precipitate is formed until it has stood for a time. Keep all solutions cold. Louis E. Preiss.

REVIEWS.

A Text-Book of Inorganic Chemistry. By Dr. A. F. Holleman, Professor Ordinarius in the University of Groningen, Netherlands. Rendered into English by Hermon C. Cooper, Ph.D., Instructor in Syracuse University, with the co-operation of the author. First edition, first thousand. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. 1902. pp. 458.

The German edition of this book has been so recently reviewed in this Journal[1] that it only remains to call attention to the appearance of the American edition. Stress should be laid upon the fact that this book is not meant for beginners, and whoever places it in the hands of a student in the earlier stages of his work makes a fatal mistake. The reviewer's opinion of the book has already been expressed, and he wishes to congratulate Dr. Cooper upon the completion of the long and arduous task involved in bringing out the English edition of a work of this size. H. C. J.

[1] This Journal, **27**, 159 (1902).

Thermodynamique et Chimie. Leçons élémentaires a l'Usage des Chimistes. Par P. Duhem, Correspondent de l'Institut de France. Professeur de Physique Théorique a L'Université de Bordeaux. Paris, Librarie scientifique A. Hermann. pp. 496. 1902.

The authority of Duhem in the field of thermodynamics, especially as applied to chemistry, is well recognized. His "Traité Élémentaire de Mécanique Chimique Fondée sur la Thermodynamique" has contributed much towards placing chemical mechanics upon an exact basis. The present work is far more elementary, avoiding the use of the higher mathematics.

Some of the more important subjects dealt with are work and force, quantity of heat and internal energy, chemical calorimetry, the principles of chemical statics, the phase rule, polyvariant systems, the displacement of equilibrium, bivariant systems—the indifferent point, mixed crystals, isomorphous mixtures, the critical conditions, chemical mechanics of perfect gases, chemical dynamics and explosives.

The work is written in that clear and concise style which is characteristic of the author, and is a valuable addition to the literature of chemical dynamics and equilibrium.

One statement in the preface seems to call for special comment. There are those who will differ from Duhem when he states that "nous n'avons voulu ni oublier, ni laisser oublier, que l'union de la Thermodynamique et de la Chimie s'etait accomplir en France, au laboratoire de l'immortel Henri Sainte-Claire Deville." While it is true that Deville carried out valuable experimental work in this field, it is also true that his theoretical deductions from his own work have been shown to be largely erroneous. In this connection the name of Horstmann should always be given the first place, since it was he who first successfully applied the mechanical theory of heat to chemical processes.   H. C. J.

The Elements of Physical Chemistry. By J. Livingston R. Morgan, Ph. D., Adjunct Professor of Physical Chemistry, Columbia University. Second edition, revised and enlarged; first thousand. New York : John Wiley & Sons ; London : Chapman & Hall, Limited. pp. 344. 1902.

The appearance of the first edition of this book has already been noticed in this Journal.[1] The author states in his preface to the second edition that "in preparing this edition I have endeavored to do three things : First, to bring the subject-matter itself up to date ; second, to make, wherever possible, the relations clearer than before ; and third, to make the book itself more useful to those studying the subject without an instructor. * * * Many things found superfluous

[1] This Journal, **21**, 459.

in the old edition have been omitted and a number of new relations added.''   H. C. J.

THE PRINCIPLES OF INORGANIC CHEMISTRY. By WILHELM OSTWALD. Translated with the author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., PH.D. With 122 figures in the text. London : Macmillan & Co., Limited ; New York : The Macmillan Co. 1902. pp. 785.

The German edition of this work has been reviewed in this JOURNAL.[1] It only remains to call attention to the appearance of the English edition of this important book. It is not too much to predict that this treatise on inorganic chemistry from the standpoint of physical chemistry, written by the master hand of Ostwald, will materially modify the teaching and study of this all-important branch of chemistry.

It is not at all clear to the reviewer why so little stress has been laid upon the Periodic System, since this generalization has certainly contributed much to the scientific study of inorganic chemistry.

The work of the translator, on the whole, is very well done. A few expressions which could have been improved upon have crept in, such as '' Quantity Relations,'' and '' with all the accuracy with which we can endow the measurement'' on page 39 ; and '' Other Methods of Preparation of Hydrogen'' on page 83. When, however, we consider the large amount of drudgery which is involved in translating a work of this size, we heartily congratulate the translator upon the successful completion of his task.   H. C. J.

INTRODUCTION A L'ÉTUDE DE METAUX, LEÇONS PROFESSÉES A LA FACULTÉ DES SCIENCES. Par ALFRED DITTE, Professeur de Chemie a l'Université de Paris. Paris : Société d'Éditions Scientifiques. 1902. pp. ii + 488.

In looking over this volume one is very strongly reminded of Wurtz's famous phrase : '' La Chemie est une Science Francaise.'' This statement is not very far from the truth in the particular field which the book covers, particularly of that portion of it treating of the properties of metals, and it is not surprising to see the names of so many French investigators in this subject. The subject has been attractive in itself, and the study of the properties of metals and alloys has been fostered by the Society for the Encouragement of National Industry. Under this influence the knowledge of the properties of metals has been greatly extended, notably by the beautiful researches of Osmond, Le Chatelier, Charpy, and others.

The subject is presented in a manner essentially different from the way it would be presented in any other language.

[1] This JOURNAL, **25**, 83.

The tendency of the present day to specialize is so great that it is somewhat surprising to see a book attempting to cover so wide a field. The author begins with the minerals as they come from the earth and traces the history of the changes which a metal may be subjected to until it again returns to the earth. Surely, a very wide field.

As far as the reviewer is able to judge such an extensive subject, the ground is well covered, except that the author has suffered from a certain amount of provincialism which has allowed him in many cases to accept the French workers as authority and to allow the important work of others to pass unmentioned. It might perhaps be better to say that the author has so selected his subjects as to confine himself largely to the French investigators, but the whole book would have been more valuable if the researches of foreign workers had been given greater consideration. As it is the book contains perhaps a greater number of interesting facts in regard to the properties of metals, exclusive of books devoted to iron and steel, from the purely scientific point of view than any other one volume.

The book is divided into two parts: I. The metals considered among themselves; II. the metals in their relations to other substances. In the first part is considered the natural occurrence and origin of minerals, the preparation of artificial minerals which has been investigated almost solely by the French, the concentration of ores and the various metallurgical processes, and of the properties of the metals themselves there is discussed the isomeric modification of metals, and the more general properties such as fusibility, conductivity for heat and electricity, magnetism, tenacity, ductility, etc., and the causes which modify these properties.

In the second part the author treats of the properties of alloys and the study of their constitution by means of the microscope, their fusibility and electrical conductivity curves, and the more general properties of various alloys of iron, nickel, copper, etc. The action of various elementary gases and other elements, acids, bases, and salts, with special emphasis on the thermo-chemistry of the reactions are described; also the effect of atmospheric agencies on metals and alloys, and, finally, the various classifications of the elements into natural systems.

The book is very attractively issued, but its value would have been greatly increased had it been provided with a more serviceable index.   HENRY FAY.

AMERICAN

CHEMICAL JOURNAL

ON SOME DOUBLE AND TRIPLE THIOCYANATES.

I. Introduction.

By. H. L. Wells.

Several investigations, dealing chiefly with the double salts of caesium thiocyanate with a number of other thiocyanates, were undertaken in this laboratory during the past winter. This work was taken up because comparatively few double thiocyanates were known, and since several of those which had been described appeared to have compositions at variance with the known double chlorides, bromides, and iodides. After a number of double salts had been prepared, some of which proved to be unusually interesting, a very remarkable triple thiocyanate was accidentally made.

This triple salt was of so much interest that our original plans were considerably modified and much attention was then given to the preparation of other triple salts.   Work was continued, however, on such double salts as might possibly throw light upon the nature of the curious triple salts.

The work with the triple thiocyanates, as far as it has gone,

shows that these compounds exist in great variety, and that a practically new, and probably important, field of inorganic chemistry has been opened up by their discovery.

The object of this introduction is to present the results thus far obtained in a concise form and to discuss them to some extent. Since the experimental details are given in subsequent articles, it may be mentioned here that no product has been accepted as a chemical compound that was not well and homogeneously crystallized, and that every formula depends upon analyses of at least two separate crops of crystals.

Twenty-three double salts, all but one of which are believed to be new, and 14 triple salts are to be considered.

The first research that will be mentioned is that of Mr. W. K. Wallbridge, who made experiments with solutions of caesium and ferric thiocyanates. After a thorough investigation he found but one double salt,

$$3CsSCN.Fe(SCN)_3.2H_2O.$$
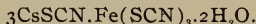
This may be called caesium ferrisulphocyanide, for it corresponds to the ferricyanides in type, and, moreover, Professor Walden, of Riga, has called attention[1] to the resemblance to the complex cyanides of some double thiocyanates partially investigated by him, probably having the formulas

$$K_4Co(SCN)_6.6H_2O, \qquad K_4Mn(SCN)_6.3H_2O,$$
$$and \ K_2Zn(SCN)_4.3H_2O.$$

Krüss and Moraht[2] have described the salt

$$3KSCN.Fe(SCN)_3,$$
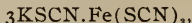
and a corresponding ammonium salt. These products were obtained by evaporating practically to dryness solutions of the constituents in the required proportions over sulphuric acid. They are described as exceedingly hygroscopic, so that it was impossible to weigh out samples of them, and the water in them, if any, was not determined. If it were not for their analogy with our caesium salt, which is not hygroscopic, and with Rösler's chromium salts,[3]

[1] Ztschr. anorg. Chem.. **23**, 373 (1900).
[2] Ann. Chem. (Liebig), **260**, 206 (1890).
[3] *Ibid.*, **141**, 195 (1867).

$$(NH_4)_3Cr(SCN)_6.4H_2O, \qquad Na_3Cr(SCN)_6.7H_2O,$$
$$K_3Cr(SCN)_6.4H_2O, \qquad and \quad Ag_3Cr(SCN)_6,$$
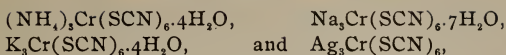
the reasons for accepting these products as real chemical compounds would appear insufficient. Krüss and Moraht described also $9KSCN.Fe(SCN)_3.4H_2O$, as well as the ammonium, sodium, and lithium salts corresponding exactly to these, even to the same amount of water. These products also were obtained by evaporating practically to dryness solutions of the constituents in the required proportions. It is true that these investigators say that they recrystallized the products; but in one case at least the product was a hard crust, and their descriptions show that these salts were so hygroscopic that the mother-liquors, if there were any, could have differed but little from the solids. Krüss and Moraht state that the sodium salt, the most satisfactory one of the lot, occurred in crystals of two kinds, rhombohedra and hexagonal prisms. This is good evidence of the presence of a mixture. It seems probable, therefore, that insufficient ground exists for accepting these salts with the extraordinary ratio of $9:1$. Krüss and Moraht were led to believe in the existence of these salts from the fact that the colors of certain ferric salt solutions deepened until 12 molecules of an alkaline thiocyanate had been added; but this phenomenon may now be explained, to some extent at least, by the effect of mass-action in retarding the ionization of ferric thiocyanate.

Mr. Wallbridge experimented also with caesium-lead and potassium-lead thiocyanates, and I have independently confirmed the composition of two of his salts. We have prepared the compounds

$$3CsSCN.Pb(SCN)_2,$$
$$KSCN.Pb(SCN)_2,$$
and $\qquad 6KSCN.Pb(SCN)_2.2H_2O.$
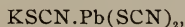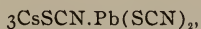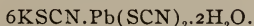
The finding of two potassium salts and only one caesium compound, while all of them are of different types, is somewhat remarkable, but we have made many unsuccessful efforts to prepare other caesium salts. The compound $KSCN.Pb(SCN)_2$ corresponds to the most common type of lead double halides,

while the other two salts represent new types as far as lead is concerned ; in fact, the 6 : 1 salt is without parallel among the established double salts of all kinds, and, on this account, it is of great interest. There is no doubt about the existence of this 6 : 1 salt, for it forms good crystals which are stable in the air and are entirely different in appearance from the constituent salts, and we have prepared and analyzed two entirely independent crops of it.

Mr. H. S. Bristol investigated the combinations of caesium and mercuric thiocyanates, and I have extended the experiments considerably in vainly attempting to prepare other double salts. He found only the two salts,

$$2CsSCN.Hg(SCN)_2.H_2O$$
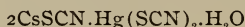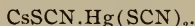
and $\qquad CsSCN.Hg(SCN)_2.$

These compounds correspond in type to known double halides, for instance, $2KCl.HgCl_2.H_2O$ and $CsCl.HgCl_2$; moreover, Fleischer[1] has described the salt $2NH_4SCN.Hg(SCN)_2$, which agrees with the first caesium thiocyanate except in regard to water. The striking result of this investigation is the small number of caesium-mercuric thiocyanates as compared with the chlorides, bromides, and iodides, for all of the latter are known in four or five types, as, for example, Cs_3HgCl_5, Cs_2HgCl_4, Cs_2HgCl_3, $CsHg_2Cl_5$, and $CsHg_5Cl_{11}$.[2]

Mr. C. S. Leavenworth has experimented with mixtures of caesium and manganous thiocyanates with the result that he was able to prepare but one salt,

$$4CsSCN.Mn(SCN)_2,$$

under widely varying conditions. This is evidently caesium manganothiocyanate, analogous to Walden's salt,

$$K_4Mn(SCN)_6.3H_2O,$$

which has been mentioned previously.

Mr. R. T. Roberts has made a careful series of attempts to make a caesium-nickel thiocyanate, but without success, for upon allowing solutions containing the two salts in various proportions to evaporate at ordinary temperatures only indefi-

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[1] Ann. Chem. (Liebig), **179**, 225 (1875).
[2] Am. J. Sci., **44**, 221 (1892).

nite mixtures were obtained. In this case the thiocyanates show less tendency to form double salts than the chlorides and bromides, although no caesium-nickel iodide could be made by Campbell,[1] who attempted its preparation in this laboratory several years ago.

Mr. Roberts studied also the results obtained by dissolving cuprous thiocyanate in caesium thiocyanate solutions, and obtained only the salt

$$CsSCN.CuSCN.$$

After many attempts he did not succeed in preparing Thurnauer's[2] salt, $6KSCN.CuSCN$, and, while Thurnauer himself was uncertain whether this was a double salt or a mixture, we are convinced that the latter was the case.

I found that silver thiocyanate is much more prolific than the cuprous compound in the formation of double salts with caesium thiocyanate, for in a systematic investigation of the matter I have prepared the salts

$$3CsSCN.AgSCN,$$
$$2CsSCN.AgSCN,$$

and $\qquad CsSCN.AgSCN.$
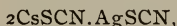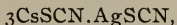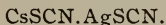
Mr. H. F. Merriam found that three potassium salts,

$$3KSCN.AgSCN,$$
$$2KSCN.AgSCN,$$

and $\qquad KSCN.AgSCN,$
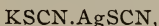
could be easily prepared, corresponding exactly in composition with the caesium compounds. The 1 : 1 potassium-silver salt has been previously described by Hull,[3] while Fleischer[4] has prepared the corresponding ammonium salt,

$$NH_4SCN.AgSCN.$$

It should be noticed that whereas only one caesium-cuprous thiocyanate could be prepared, three caesium-cuprous chlorides are known. This is another case where the thiocya-

[1] Am. J. Sci., **48**, 418 (1894).
[2] Ber. d. chem. Ges., **23**, 770 (1890).
[3] Ann. Chem. (Liebig), **76**, 96 (1850).
[4] *Ibid.*, **179**, 232 (1875).

nates show less variety of double salts than the halides. On the other hand, the double thiocyanates of silver show a type, the 3 : 1, which is not known among the chlorides and iodides. This apparent exception is probably due to the fact that the double chlorides, bromides, and iodides of silver have not been thoroughly investigated.

While preparing some triple salts, Mr. Merriam encountered the well-crystallized compound

$$2CsSCN.Ca(SCN)_2.3H_2O.$$
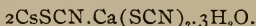
He afterwards prepared the salts

$$2CsSCN.Sr(SCN)_2.4H_2O,$$

and $\qquad 2CsSCN.Mg(SCN)_2.2H_2O.$
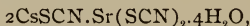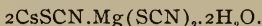
The calcium and strontium salts are of unusual interest, because double halides of the alkali metals with barium, strontium, or calcium have been unknown heretofore.[1] The solubility of these two salts increases from the calcium to the strontium compounds, and, although I have made many attempts to prepare a caesium-barium thiocyanate, no satisfactory product has been obtained.

The magnesium salt, $2CsSCN.Mg(SCN)_2.2H_2O$, is remarkable since it differs in type from all the known double halides of magnesium, which are invariably 1 : 1 salts, usually with 6 molecules of water, *e. g.*, $KCl.MgCl_2.6H_2O$. It is interesting, however, to notice that this double thiocyanate of magnesium agrees exactly with the zinc salt which is to be considered immediately.

I have made a thorough investigation with caesium and zinc thiocyanates, and have obtained only the salt

$$2CsSCN.Zn(SCN)_2.2H_2O.$$
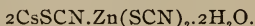
The thiocyanates are here not as prolific as the chlorides and bromides, which yield 3 : 1 and 2 : 1 anhydrous salts. I obtained also the salt

$$Zn(SCN)_2.2AgSCN.$$
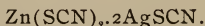
[1] A potassium-barium nitrite, $K_2Ba(NO_2)_4.H_2O$, and similar strontium and calcium salts have been prepared by Lang (Jsb., 1862, p. 101). Up to the present time these have been, apparently, the only double salts of any kind with alkali and alkaline earth metals, but I have recently prepared a beautifully crystallized, stable double chloride, $2CsCl.CaCl_2.2H_2O$, which will be described in a future article.

Mr. Merriam and I have prepared the double salts

$$Ba(SCN)_2.2AgSCN.2H_2O,$$
$$Sr(SCN)_2.2AgSCN.2H_2O,$$
and $$Ca(SCN)_2.2AgSCN.2H_2O,$$
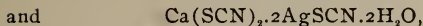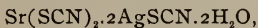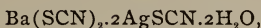
which form a striking analogous series.

In attempting to prepare a triple salt with the thiocyanates of caesium, barium, and thallium, I obtained, instead of a triple compound, the interesting double salt,

$$CsSCN.4TlSCN.$$
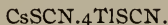
This salt is remarkable, not only because it belongs to the 1 : 4 type which is unknown among the double halides (although 4 : 1 salts are known with negative metals that are not univalent),[1] but especially because thallium in the thallous state has not been known to show any tendency to enter into complex negative radicals. For example, it is well known that thallous iodide is very insoluble in strong solutions of potassium iodide. Thallous thiocyanate, however, which is considerably soluble in water, especially when hot, dissolves also in hot concentrated solutions of caesium thiocyanate, and the double salt crystallizes out upon cooling. This happens even when a large excess of barium thiocyanate is present in the solution.

The double thiocyanates which we have studied correspond in general to the double halides, and, although two new types appear among them, there is no reason to suppose that these types of double halides will not be prepared in the future. The conclusion that I have previously arrived at,[2] namely, that the valency of the negative metal has little or no influence upon the types of double halides formed by it, appears, therefore, to apply also to the double thiocyanates.

Mr. O. G. Hupfel made the original attempt to prepare caesium-silver thiocyanates, which have been mentioned previously, but, in preparing caesium thiocyanate from caesium carbonate and barium thiocyanate, an excess of the latter salt remained in the product, and when silver thiocyanate was

dissolved in a concentrated solution of this mixture, magnificent crystals were produced upon cooling. These proved to be a triple salt of the curious composition represented by the formula

$$3CsSCN.2AgSCN.Ba(SCN)_2.$$

To Mr. Hupfel belongs the credit of making a very interesting accidental discovery, but he was unable, from lack of time, to study the matter further. I undertook, therefore, to thoroughly investigate the products produced from solutions containing the three constituent salts in widely varying proportions. As a result it was found that this triple salt was formed under very wide limits of conditions. It was shown also that, although the compound is decomposed by much water, it is capable of being recrystallized from about its own weight of that liquid.

Then I prepared the analogous salt,

$$3CsSCN.2CuSCN.Ba(SCN)_2.$$

This is also a beautifully crystallized compound, but it is incapable of being recrystallized without filtration on account of the fact that cuprous thiocyanate is more sparingly soluble than the silver salt in concentrated solutions of the other thiocyanates. I was unsuccessful in attempting to introduce thallous, aurous, and mercurous thiocyanates in the place of the silver and cuprous salts.

Mr. Merriam prepared the strontium salts,

$$3CsSCN.2AgSCN.Sr(SCN)_2,$$

and $\qquad 3CsSCN.2CuSCN.Sr(SCN)_2,$
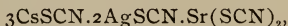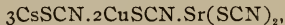
which are practically identical in appearance and behavior with the barium compounds.

The four triple salts just mentioned are isomorphous, forming tetragonal crystals with steep pyramids and resembling the mineral apophyllite. It is expected that a description of the crystals will be published elsewhere by Mr. J. C. Blake.

Mr. Merriam prepared a caesium-silver-calcium thiocyanate, which formed beautiful crystals and was capable of being recrystallized from a small quantity of water, but it showed a

form and composition differing from the barium and strontium salts, and corresponded to the formula

$$2CsSCN.2AgSCN.Ca(SCN)_2.2H_2O.$$
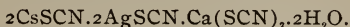
Mr. Merriam made also the salt

$$2CsSCN.2AgSCN.Mg(SCN)_2.2H_2O,$$

which can be recrystallized from water and forms coherent masses of small crystals. It is very remarkable that the calcium salt agrees in type with the magnesium rather than with the barium and strontium compounds.

Mr. Leavenworth and I prepared and analyzed the manganese salt,

$$2CsSCN.2AgSCN.Mn(SCN)_2.2H_2O.$$

This salt also can be recrystallized unchanged.

Mr. Roberts and I obtained the salts

$$2CsSCN.2AgSCN.Ni(SCN)_2.2H_2O,$$

and $\quad\quad 2CsSCN.2CuSCN.Ni(SCN)_2.2H_2O.$
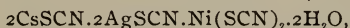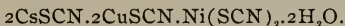
These two salts are very difficultly soluble in water, and, since much water decomposes them, it is impossible to recrystallize either of them without the use of an excess of soluble thiocyanates.

I have made an elaborate study of the caesium-silver-zinc thiocyanates. In this case, for the first time, more than one triple salt was encountered, and it is remarkable that none of the four salts obtained corresponds in type with those previously mentioned. These compounds are:

$$CsSCN.AgSCN.Zn(SCN)_2.H_2O,$$
$$2CsSCN.AgSCN.Zn(SCN)_2,$$
$$CsSCN.3AgSCN.2Zn(SCN)_2,$$

and $\quad\quad CsSCN.4AgSCN.2Zn(SCN)_2.$
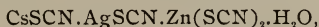
These are all well crystallized salts which are too insoluble to be recrystallized from water without decomposition.

I have prepared also a beautifully crystallized potassium salt,

$$4KSCN.2AgSCN.Ba(SCN)_2.H_2O.$$
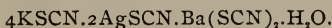
It is astonishing that this salt, which can be recrystallized from water, differs from the caesium-silver-barium salt, as well as from all the others.

The fourteen triple salts that have been mentioned belong to seven different types:

I. One salt, $CsAgZn(SCN)_4.H_2O.$
II. One salt, $Cs_2AgZn(SCN)_5.$
III. Five salts, corresponding to $Cs_2Ag_2Ca(SCN)_6.2H_2O.$
IV. Four salts, corresponding to $Cs_3Ag_2Ba(SCN)_7.$
V. One salt, $K_4Ag_2Ba(SCN)_8.H_2O.$
VI. One salt, $CsAg_3Zn_2(SCN)_8.$
VII. One salt, $CsAg_4Zn_2(SCN)_9.$

The first of these salts might be considered to be a derivative of $Cs_3Ag(SCN)_4$ by the replacement of two caesium atoms by zinc, but a theory of this kind is inapplicable to most of the other types.

The salt $Cs_2Ag_2Mn(SCN)_6.2H_2O$, belonging to type III., might be regarded as a double manganosulphocyanide, analogous to $K_2Na_2Fe(CN)_6.8H_2O$ and $K_2BaFe(CN)_6.3H_2O$, but such a view does not apply to the other types.

The view that these triple salts are compounds of two double salts is also untenable, as far as most of the types are concerned, unless unknown double salts are assumed, although the first salt might be supposed to be composed of

$Cs_2Zn(SCN)_4$ and $Ag_2Zn(SCN)_4$,
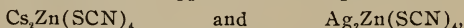
water of crystallization being left out of consideration.

It does not appear that the water of crystallization present in three of the types bears any relation to their composition in replacing other constituents, although it might be assumed that H_2O in I., or $2H_2O$ in III., took the place of one CsSCN in II. and IV.

The arguments which have just been advanced indicate that the triple thiocyanates are not derived from double salts in any simple manner, either by substitution or combination. They must be regarded, therefore, as being built up from simple salts and be viewed as molecular combinations of the same nature as double salts, but more complex than the latter.

It may be mentioned that experiments with lead and mercuric thiocyanates have failed to give me any triple salts with caesium and silver thiocyanates, but the amount of work still to be done on triple thiocyanates is very great. No rubidium, ammonium, sodium, or lithium salts have as yet been investigated, nor has any attempt been made to prepare salts with cobalt, cadmium, and several other bivalent metals. Moreover, it is probable that among the cyanides, fluorides, chlorides, bromides, and iodides, as well as the sulphates, thiosulphates, and other oxygen salts, interesting triple compounds will be found. There is no doubt, as will be evident from the examples, to be given presently, of the few triple salts already known, that these compounds are formed with other groups than the two univalent metals and one bivalent metal present in the thiocyanates under consideration.

It is hoped that the future work which has just been outlined, and which will be industriously carried out in this laboratory, may lead to some insight into the laws of complex molecular combination.

In connection with the triple thiocyanates, attention may be called to a few other triple salts which are known. The compounds which may be regarded as double ferrocyanides, or also as triple cyanides, such as $2KCN.Ba(CN)_2.Fe(CN)_2.3H_2O$ (Bunsen), and which have been mentioned previously, are known in considerable variety. Besides these there are combinations of cyanides and other salts, for example, $4KCN.Mn(CN)_2.2KCl$ (Descamps), $4NH_4CN.Fe(CN)_2.2NH_4Cl.3H_2O$ (Bunsen), $4KCN.Fe(CN)_2.3Hg(CN)_2.4H_2O$ (Kane), $3NH_4CN.KCN.Fe(CN)_2.2NH_4Cl$ (Étard and Bémont), $4KCN.Fe(CN)_2.2NaNO_2.2KNO_3$ (Martius).[1] The last two salts appear to be quadruple. Probably the best known triple salts are the nitrites,

$$K_2BaNi(NO_2)_6,$$
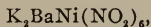
and the corresponding strontium and calcium compounds.[2] These salts may be considered as analogous to the ferrocya-

[1] References to these compounds are in Beilstein's "Handbuch."

[2] Lang : Jsb., (1862) p. 101 ; Hampe : *Ibid.*, (1863), p. 163 ; Künzel(Erdmann) : Fres. Ztschr., **3**, 161 ; Erdmann : J. prakt. Chem., **97**, 395.

nides, particularly since the double salt $K_4Ni(NO_2)_6$ is known. Walden,[1] of this laboratory, has described the salts $KBr.FeBr_2$. $2FeBr_3.3H_2O$ and $RbBr.FeBr_2.2FeBr_3.3H_2O$. Many years ago Bonsdorff[2] described the compound $6KCl.CuCl_2.3HgCl_2.2H_2O$, and recently Mr. Merriam, of this laboratory, has prepared it, and by a partial analysis has confirmed Bonsdorff's results. The minerals pachnolite, $NaF.CaF_2.AlF_3.H_2O$, and polyhalite, $K_2SO_4.2CaSO_4.MgSO_4.2H_2O$, are triple salts. The minerals thaumasite, $CaCO_3.CaSiO_3.CaSO_4.15H_2O$, and sulphohalite, $2Na_2SO_4.NaCl.NaF$, are cases of triple salts with different acid radicals, while hanksite, $9Na_2SO_4.2Na_2CO_3.KCl$, has an additional complication in containing two metals, and northuptite, $MgCO_3.Na_2CO_3.NaCl$, is a triple salt with only two metals and two acids.

Enough examples have been given to show that triple salts exist in considerable variety. It seems probable that these compounds and double salts are governed by the same laws, and that a more thorough knowledge of the more complicated substances may be of assistance in explaining the simpler class.

The more important results of these investigations are :

1. The description of numerous double thiocyanates, among which the salts $6KSCN.Pb(SCN)_2$ and $CsSCN.4TlSCN$ present novel types, while the alkali metal salts with strontium and calcium show that the alkaline earth metals enter into complex negative radicals more readily than has been supposed.

2. The conclusion, from the study of several series of salts, that the thiocyanates generally form double salts in smaller variety than the halides.

3. The discovery of the existence of triple thiocyanates of various types, and particularly the preparation of four distinct triple salts from the thiocyanates of caesium, silver, and zinc.

II. Caesium-Ferric Thiocyanate.

By William K. Wallbridge.

Caesium thiocyanate was prepared by boiling a solution of

[1] Am. J. Sci., **48,** 289 (1894).
[2] Pogg. Ann., **33,** 81 (1834).

the ammonium salt with the proper quantity of caesium carbonate until no more ammonium carbonate was given off, and crystallizing the product. A solution of the ferric salt was made by mixing solutions of the required proportions of ferric sulphate and barium thiocyanate, and filtering.

Two solutions were used for the experiments. In the first case ferric thiocyanate was added in small quantities at a time to a solution of 50 grams of caesium thiocyanate, while in the other case caesium thiocyanate was gradually added to a solution of 30 grams of ferric thiocyanate, calculated as the anhydrous salt. After each addition the solution was evaporated in the air or over sulphuric acid until crystals formed, or until it was evident that no satisfactory crystals could be obtained. In the solution containing an excess of the caesium salt, the latter crystallized out, in a pure, or nearly pure condition, until about 15 grams of ferric thiocyanate had been added, when a well crystallized double salt was obtained (analysis I.). Another crop (analysis II.) was prepared by evaporating the mother-liquor. No satisfactory crystals were obtained from the solution containing an excess of ferric thiocyanate until about 24 grams of the caesium salt had been added, when a crop of the same salt as that obtained from the other solution was formed (analysis III.).

These experiments indicate that only one caesium-ferric thiocyanate can be prepared. The results show that this salt has a composition corresponding to the formula $Cs_3Fe(SCN)_6.$ $2H_2O$. It crystallizes in dark, opaque, tabular crystals, often about a centimeter in diameter. The crystals have a beautiful bronze luster and are perfectly stable in the air, although they are exceedingly soluble and are formed only in very concentrated solutions. The following analyses were made:

	Calculated for $Cs_3Fe(SCN)_6.2H_2O$.	I.	Found. II.	III.
Cs	47.56	46.77	....	....
Fe	6.67	6.97	....	7.71
SCN	41.48	41.39	41.27	42.48
H_2O	4.29	....	....	....

In these analyses iron was weighed as the oxide after pre-

cipitation with ammonia, caesium was weighed as the normal sulphate, and sulphocyanogen was determined by the usual volumetric method, usually in a separate sample of the salt.

III. The Caesium-Lead and Potassium-Lead Thiocyanates.

By W. K. Wallbridge and H. L. Wells.

3 : 1 Caesium-Lead Thiocyanate, $Cs_3Pb(SCN)_5$.—Two series of experiments were carried out with caesium thiocyanate and lead thiocyanate. In the first case about 5 grams of the lead salt were dissolved in a hot concentrated solution of 50 grams of the caesium salt. At first, crystals of lead thiocyanate were deposited upon cooling, but after further concentration a double salt was obtained (analysis I. by Wallbridge). Further additions of the lead salt and variations in the concentration failed to give any other double salt. For the second set of experiments 180 grams of caesium thiocyanate and 20 grams of the lead salt were dissolved in water, and, upon concentrating and cooling, a beautiful crop of the double salt was obtained. Another crop was prepared from the mother-liquor by further concentration, and still another after adding 5 grams more of lead thiocyanate (analyses II., III., and IV. by Wells). The results of the analyses are as follows:

	Calculated for $Cs_3Pb(SCN)_5$.	I.	II.	III.	IV.
Cs	44.53	45.26	....	....	....
Pb	23.10	21.95	22.20	22.77	23.05
SCN	32.37	31.52	32.71	32.53	32.39

This salt forms colorless, transparent massive crystals, which are apparently monoclinic in form. Some of the crystals obtained were nearly 1 cm. in diameter. The salt is stable when exposed to the air. It requires the presence of an excess of caesium thiocyanate for its formation, hence it cannot be recrystallized from water unless a part of the lead salt is removed by filtration.

1 : 1 Potassium-Lead Thiocyanate, $KPb(SCN)_3$.—When 5 grams of lead thiocyanate were dissolved in a boiling concentrated solution of 30 grams of the potassium salt a crop of

small, brilliant crystals was obtained upon cooling. They were carefully dried on paper, then air-dried (analysis I.). The mother-liquor was diluted slightly, 5 grams more of lead thiocyanate were dissolved in it by heating, and another crop was obtained by cooling (analysis II.). The analyses (by Wallbridge) are as follows:

	Calculated for KPb(SCN)₃.	I.	Found. II.
K	9.31	9.56	....
Pb	49.27	48.48	50.50
SCN	41.42	41.15	40.57

This salt forms small, brilliant, white crystals, which are usually less than 1 mm. in diameter. It is stable in the air, but is decomposed by water.

6 : 1 Potassium-Lead Thiocyanate, $K_6Pb(SCN)_8.2H_2O$.—A crop of this salt was prepared by allowing the mother-liquor from crop II. of the preceding salt to stand for nearly two weeks exposed to the air at the ordinary temperature (analysis I. by Wallbridge). Another crop was prepared by dissolving 50 grams of potassium thiocyanate and 3 grams of the lead salt in a little hot water, and allowing the liquid to evaporate at ordinary temperature for several days (analysis II. by Wells). The analyses, which were made of material which was carefully dried by pressing between filter-papers and then air-dried, are as follows:

	Calculated for K₆Pb(SCN)₈.2H₂O.	I.	Found. II.
K	24.91	24.80	....
Pb	21.98	22.20	22.02
SCN	49.28	49.07	49.09
H₂O	3.82	3.50	....

This salt occurs in white, opaque, prismatic crystals which are stable in the air. The crystals usually grow together and form a peculiar net-work at the bottom of the vessel in which they crystallize. Portions of this net-work of considerable size can be readily removed from the liquid. The individual prisms are about 1 mm. in diameter and several millimeters in length.

In analyzing the double salts of lead, the latter metal and

the alkali metals were weighed as sulphates, while sulpho-cyanogen was determined in separate samples by titration.

Attempts were made to prepare ammonium-lead thiocyanates, but these were entirely without success.

IV. The Caesium-Mercuric Thiocyanates.

By H. S. Bristol.

2 : 1 Caesium-Mercuric Thiocyanate, $Cs_2Hg(SCN)_4.H_2O$.— This salt is formed under a very wide range of conditions by cooling hot solutions of the component salts. The solution may be almost saturated with the caesium salt and contain about 20 parts by weight of the latter to 1 part of the mercuric salt, or the solution may be much more dilute and contain nearly as much of the mercuric as of the caesium salt. Crop I. was made from 160 grams of caesium thiocyanate and 12 grams of mercuric thiocyanate in a volume of about 500 cc. ; crop II. from 160 grams caesium thiocyanate, and 24 grams mercuric thiocyanate in a volume of about 1000 cc. Many other crops were prepared, under widely varying conditions, which were identified by closely agreeing determinations of sulphocyanogen. The analyses are as follows :

	Calculated for $Cs_2Hg(SCN)_4.H_2O$.	Found. I.	II.
Cs	37.15	37.22	37.42
Hg	27.93	27.76	27.95
SCN	32.41	32.35	32.86
H_2O	2.51	....	2.25

This salt forms large, somewhat flattened, white prisms, which often grow together in parallel position. It is rather freely soluble in water, especially upon warming, and it may be recrystallized unchanged. It melts between 168° and 170°.

1 : 1 Caesium-Mercuric Thiocyanate, $CsHg(SCN)_3$. — This salt is produced from solutions containing comparatively little caesium thiocyanate, which are nearly saturated with the mercuric salt. A crop thus made gave the following results on analysis :

	Calculated for $CsHg(SCN)_3$.	Found I.
Cs	26.23	25.99
Hg	39.45	39.44
SCN	34.32	34.22

Three other crops were identified by titrating the sulpho-cyanogen not combined with mercury, with the following results:

	Calculated	II.	Found III.	IV.
SCN(with Cs)	11.44	11.15	11.51	11.64

This salt forms large colorless crystals which are often of a pyramidal habit and highly modified with faces. It is difficultly soluble, even in hot water.

No indications of the existence of other double salts were obtained, although it is believed that the search for them was very thorough.

In making the analyses of the two salts, mercury was weighed in a Gooch crucible as sulphide, caesium was weighed as normal sulphate, while sulphocyanogen was determined by titration according to Volhard's method. Where the total sulphocyanogen was determined by this method the mercury was always previously removed by the action of hydrogen sulphide in cold, dilute solution. The observation of Cohn[1] that mercuric thiocyanate is not acted upon in this titration was made use of very satisfactorily in determining occasionally the sulphocyanogen combined with caesium.

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V. Caesium-Manganous Thiocyanate, $Cs_4Mn(SCN)_6$.

By C. S. Leavenworth.

Only one double salt was obtained by systematic experiments with solutions of caesium and manganous thiocyanates. A solution of manganous thiocyanate was prepared by dissolving the carbonate in dilute thiocyanic acid, the latter having been prepared by the action of hydrogen sulphide upon lead thiocyanate suspended in water, and the excess of hydrogen sulphide removed by passing air through the liquid.

To a concentrated solution of the manganous thiocyanate caesium thiocyanate was added a little at a time until, after evaporation, crystals of the double salt were formed upon cooling and standing. Another series of experiments was made by starting with a concentrated solution of caesium thio-

[1] Ber. d. chem. Ges., **34**, 3502.

cyanate and gradually adding small quantities of manganous thiocyanate. Two crops were obtained, one of rather small slender prisms, where the salt was deposited rapidly (I.), the other, by slow evaporation, in magnificent massive crystals (II.). The color is pale yellowish-green. The analyses are as follows:

	Calculated for $Cs_4Mn(SCN)_6$	Found. I.	II.
Cs	56.90	57.23	••••
Mn	5.88	5.92	6.18
SCN	37.22	36.65	37.70

In making the analyses, manganese was precipitated as the sulphide and thus separated from caesium. The sulphide was dissolved in hydrochloric acid, and the manganese was determined as the pyrophosphate by the familiar method of Gibbs. The caesium was weighed as the sulphate. Sulphocyanogen was determined in a separate portion by the usual volumetric method.

VI. Caesium-Cuprous Thiocyanate, $CsCu(SCN)_2$.

By R. T. Roberts.

This double salt is the only one that could be obtained by dissolving cuprous thiocyanate in solutions of the caesium salt and evaporating to crystallization. It is formed in cold saturated solutions of caesium thiocyanate and crystallizes beside the latter, so that it is evident that no double salt containing a greater proportion of the caesium salt can be prepared. It forms also in solutions that are not quite saturated with caesium thiocyanate, but upon diluting such solutions slightly cuprous thiocyanate precipitates.

The salt forms brilliant colorless prisms, sometimes occurring in massive groups in parallel position 4 or 5 cm. long, and 1 or 2 cm. thick. It is stable in the air, but is decomposed by water with separation of cuprous thiocyanate.

The following analyses are of different crops made under conditions which varied as much as possible. The last crop was made and analyzed by Prof. Wells.

	Calculated for CsCu(SCN)₂	Found.				
		I.	II.	III.	IV.	V.
CsSCN	61.13	60.50	60.41	60.71	61.13	61.69
CuSCN	38.87	38.69	38.53	38.89	....	38.47

Cuprous thiocyanate was determined by treating the salt with water and weighing the precipitate in a Gooch filter, while caesium thiocyanate was determined by titrating the filtrate with decinormal silver nitrate, according to Volhard's method.

Attempts to prepare potassium-cuprous and ammonium-cuprous thiocyanates were without success.

VII. The Caesium-Silver Thiocyanates.

By H. L. Wells.

The 3 : 1 Salt, $Cs_3Ag(SCN)_4$.—To a nearly saturated solution of 50 grams of caesium thiocyanate the silver salt was added in small portions and dissolved by heating. After 10 grams of the latter had been used a double salt (I.) was formed upon cooling and standing for a few hours. Another crop (II.) was obtained by dissolving 2 grams more of silver thiocyanate in the mother-liquor from the first. It forms very large, transparent, colorless crystals which are stable in the air, and have an octahedral aspect, but are evidently not isometric in form. Crystals a centimeter or more in diameter are easily grown. The following analyses were made :

	Calculated for Cs₃Ag(SCN)₄.	Found.	
		I.	II.
CsSCN	77.54	77.65	77.52
AgSCN	22.46	22.39	22.34

The 2 : 1 Salt, $Cs_2Ag(SCN)_3$.—The addition of silver thiocyanate was continued, and when 17 grams in all had been used another salt made its appearance (I.), and another crop of this (II.) was prepared by dissolving 5 grams more of the silver salt in the mother-liquor from the first. Owing to the removal of samples of the double salts for analysis and for specimens, the conditions under which this salt is formed cannot be given very exactly. It forms brilliant, transparent, colorless prisms, sometimes 2 or 3 mm. thick and a centi-

meter or more in length, and it is stable upon exposure to the air. The analyses are as follows :

	Calculated for $Cs_2Ag(SCN)_3$.	I.	Found.	II.
CsSCN	69.71	70.08		69.91
AgSCN	30.29	29.71		....

The 1 : 1 Salt, $CsAg(SCN)_2$.—The additions of silver thiocyanate were continued with the result that a heavy, syrupy liquid was obtained which for many days refused to deposit crystals. The solution was evidently supersaturated, for when at last some crystals formed and they had been dried on paper the laboratory atmosphere became impregnated to such an extent that no further difficulty was experienced in obtaining crystals from the solution. Two crops were obtained after about 36 grams of silver thiocyanate had been added altogether. The removal of previous crops had doubtless caused the loss of more caesium than silver salt from the solution, so that the proportion of silver salt present was considerably greater than that represented by the quantity added to the original 50 grams of caesium thiocyanate. It appears, therefore, that the two salts must have been present in nearly the required proportion to form this 1 : 1 salt. This double salt forms prismatic crystals of about the same size as the 2 : 1 salt, but they are more flattened and have a higher adamantine luster than the latter. The following analyses were made of two separate crops :

	Calculated for $CsAg(SCN)_2$.	I.	Found.	II.
CsSCN	53.50	54.07		53.38
AgSCN	46.50	46.29		....

The analyses were made by treating the substance with a liberal amount of water, collecting and weighing the silver thiocyanate in a Gooch crucible, and titrating the filtrate by Volhard's method. In cases where caesium thiocyanate alone was determined, the titration was made without filtering.

Caesium Thiocyanate.—This salt, which apparently has not been described, resembles the potassium compound in the appearance of its crystals. It crystallizes without water. A sample dried on paper gave 29.84 per cent. of SCN, while an-

other sample air-dried gave 30.27 per cent.; calculated for CsSCN, 30.36 per cent. The salt is exceedingly soluble in water, but it is stable in the air, except in very damp, hot weather, when it shows signs of deliquescence. For the work described in the present series of articles it was usually prepared from caesium carbonate and ammonium thiocyanate, but barium thiocyanate and caesium carbonate were also used.

VIII. The Potassium-Silver Thiocyanates.

By H. F. Merriam.

The 3 : 1 Salt, 3KSCN.AgSCN.—This compound was produced from concentrated solutions of about 50 grams of potassium thiocyanate and 15 grams of the silver salt. It forms beautiful, large, transparent, stout prisms which, after drying, gradually become opaque upon standing. This change is not due to loss of water, but depends upon some alteration in crystallization, possibly upon a splitting of the compound into one of the other double salts and potassium thiocyanate. The following analyses were made of two crops of transparent crystals and a sample (III.) which had become opaque by standing:

	Calculated for $K_3Ag(SCN)_4$.	I.	Found. II.	III.
K	25.65	25.80	....	....
AgSCN	36.30	35.83	36.42	....
Soluble SCN	38.05	38.28	37.59	38.22

The 2 : 1 Salt, 2KSCN.AgSCN.—This was obtained from concentrated aqueous solutions of about 50 grams of potassium thiocyanate and 28 grams of the silver salt. It forms magnificent, large, transparent crystals, which are perfectly stable in the air. The following analyses were obtained with three crops of the salt:

	Calculated for $K_2Ag(SCN)_3$.	I.	Found. II.	III.
K	21.71	21.72	....	....
AgSCN	46.08	....	46.45	....
Soluble SCN	32.21	32.62	32.33	32.24

The 1 : 1 Salt, KSCN.AgSCN.—A crop of this salt was prepared by adding 5 grams of silver thiocyanate to the mother-

liquor from the preceding salt. It crystallizes in very thin, diamond-shaped plates, which by slow growth sometimes attain a diameter of about a centimeter. The following analyses were made :

	Calculated for KAg(SCN)$_2$.	I.	II.
K	14.86	14.88	....
AgSCN	63.10	62.38	....
Soluble SCN	22.04	22.15	22.08

The analytical methods were the same as those used for the caesium salts, and were mentioned in the preceding article.

IX. THE CAESIUM-CALCIUM, CAESIUM-STRONTIUM, AND CAESIUM-MAGNESIUM THIOCYANATES.

BY H. F. MERRIAM.

The Calcium Salt, 2CsSCN.Ca(SCN)$_2$.3H$_2$O.—This was prepared by dissolving about equal weights of the two simple salts in very little water, and concentrating if necessary until the double salt appeared upon standing. The solution has a great tendency to remain in a supersaturated condition and to yield finally very small crystals, but by "seeding," good-sized crystals were grown. The salt forms colorless, transparent prisms which are stable in the air. The following analyses were made of separate crops :

	Calculated for Cs$_2$Ca(SCN)$_4$.3H$_2$O.	I.	II.
Cs	44.94	....	45.23
Ca	6.75	6.83	....
SCN	39.19	38.96	39.19
H$_2$O	9.12	....	....

The fact may be mentioned here that crystallized calcium thiocyanate has four molecules of water of crystallization instead of three as found by Meitzendorff.[1] The salt, which crystallizes in long prisms, is very hygroscopic. Samples of it were dried over sulphuric acid until the fragments just began to grow opaque on the edges; then sulphocyanogen determinations were made with the following results:

[1] Pogg. Ann., **56**, 63 (1842).

	Calculated for Ca(SCN)$_2$.4H$_2$O.	Found.
SCN	50.87	50.63, 51.29, 50.56, 50.36, 50.69

The salt becomes opaque over sulphuric acid and changes to Ca(SCN)$_2$.2H$_2$O, as is shown by the following analyses:

	Calculated for Ca(SCN)$_2$.2H$_2$O.	Found after drying 4 days.	after drying 10 days.
SCN	60.41	60.44	60.16

It is interesting to notice that the crystallized calcium thiocyanate has the same amount of water as the magnesium salt, Mg(SCN)$_2$.4H$_2$O, while it does not correspond to the salts Ba(SCN)$_2$.3H$_2$O and Sr(SCN)$_2$.3H$_2$O. Some triple thiocyanates which will be described subsequently also show agreements between the calcium and magnesium compounds with lack of analogy between the calcium and the strontium and barium salts.

The Strontium Salt, 2CsSCN.Sr(SCN)$_2$.4H$_2$O.—This was prepared by concentrating a solution of equal weights of the two thiocyanates until crystals were formed on cooling, and also by evaporating such a solution in a desiccator. It forms colorless, transparent crystals which are prismatic in habit and often form large compound groups of these crystals in parallel position. All the faces of the crystals appear to be rectangular. The following analyses were made of separate crops:

	Calculated for Cs$_2$Sr(SCN)$_4$.4H$_2$O.	Found. I.	II.
Cs	40.45	40.06	....
Sr	13.32	....	13.78
SCN	35.27	35.31	35.40
H$_2$O	10.96	....	....

The Magnesium Salt, 2CsSCN.Mg(SCN)$_2$.2H$_2$O. — This compound was prepared by slow evaporation in a desiccator of a solution containing 40 grams of caesium thiocyanate and the same quantity of magnesium thiocyanate. It forms magnificent, clear, colorless crystals which are hygroscopic. Two crops gave the following results upon analysis:

	Calculated for $Cs_2Mg(SCN)_4.2H_2O$.	Found. I.	II.
Cs	47.63	....	...
Mg	4.37	4.59	....
SCN	41.55	41.45	41.50
H_2O	6.45	....	....

X. THE CAESIUM-ZINC AND SILVER-ZINC THIOCYANATES.

BY H. L. WELLS.

Caesium-Zinc Thiocyanate, $Cs_2Zn(SCN)_4.2H_2O$.—This is the only double salt that could be produced under widely varying conditions. It was formed from solutions containing caesium and zinc thiocyanates in the molecular ratios 8 : 1, 4 : 1, 2 : 1, 1 : 1, and 1 : 2. The two crops analyzed were prepared under conditions represented by the first and last ratios. It is evident that the salt may be recrystallized from water. It forms large pyramidal groups of small colorless crystals; it is moderately soluble in water and is stable on exposure to the air. The analyses are as follows:

	Calculated for $Cs_2Zn(SCN)_4.2H_2O$.	Found. I.	II.
Cs	44.41	....	....
Zn	10.84	10.34	11.36
SCN	38.74	37.86	38.92
H_2O	6.01	....	....

The analyses show some variations, which are due to the presence of a large excess of caesium salt in the first case, and of zinc salt in the second case, in the solutions from which the crops were crystallized.

It may be mentioned that the zinc thiocyanate used was prepared in solution by the exact reaction of barium thiocyanate and zinc sulphate. We attempted to prepare it by boiling ammonium thiocyanate solution with zinc oxide, but this method was unsatisfactory on account of the obstinate retention of considerable quantities of ammonium compounds by the liquid. No crystals of zinc thiocyanate could be prepared by evaporating its solution over sulphuric acid or in the air at the ordinary temperature, but a white efflorescence was obtained, which, when apparently perfectly air-dry, gave 52.4

per cent. of SCN. This corresponds nearly to $Zn(SCN)_2$.$2H_2O$ which requires 53.46 per cent. Meitzendorff[1] described zinc thiocyanate, crystallized from alcohol, as anhydrous. He mentioned the efflorescence of its solutions, but apparently did not analyze the product.

Zinc-Silver Thiocyanate, $ZnAg_2(SCN)_4$, was prepared by dissolving 2.5 grams of silver thiocyanate in a very concentrated solution containing about 85 grams of zinc thiocyanate, calculated as the anhydrous salt. The solution takes place with difficulty, apparently on account of the insolubility of the double salt, the latter being precipitated upon slightly diluting the concentrated solution. Two crops prepared by cooling at considerably different degrees of concentration gave the following results upon analysis :

	Calculated for $ZnAg_2(SCN)_4$.	Found. I.	II.
Zn	12.74	....	....
AgSCN	64.67	63.72	64.02
Soluble SCN	22.59	22.88	23.03

The salt forms very small, brilliant, colorless, prismatic crystals which are stable in the air, and which retain their transparency when treated with cold water, but become opaque with hot water, and are completely decomposed when the water is boiled for some time.

XI. BARIUM-SILVER, STRONTIUM-SILVER, AND CALCIUM-SILVER THIOCYANATES.

BY H. L. WELLS AND H. F. MERRIAM.

Only one double salt could be prepared in each of these cases by dissolving silver thiocyanate in concentrated solutions of the other thiocyanates. The salts crystallize well, forming colorless prisms in the cases of the barium and calcium compounds, and plates in the case of the strontium salt, all of which are stable in the air. The three compounds are analogous in composition.

Barium-Silver Thiocyanate, $Ba(SCN)_2.2AgSCN.2H_2O$, was formed in very concentrated solutions containing about 50

[1] Pogg. Ann., **56**, 74 (1842).

grams of barium thiocyanate, and 40 grams of silver thio-cyanate. At first the solution remained supersaturated for several days, although it was very dense and syrupy, but after crystals had once been obtained there was no difficulty in obtaining more of them by impregnating the solution. Two crops were analyzed (by Wells):

	Calculated for $BaAg_2(SCN)_4.2H_2O$.	I.	II.
		Found.	
Ba	22.11	....	....
AgSCN	53.43	52.70	52.90
Soluble SCN	18.67	18.69	18.73
H_2O	5.79	....	....

The Strontium-Silver Salt, $Sr(SCN)_2.2AgSCN.2H_2O$, was formed when 15 grams of silver thiocyanate were dissolved in a concentrated solution of 45 grams of strontium thiocyanate, and also when larger quantities of the silver salt were used. Two crops were analyzed (by Merriam):

	Calculated for $SrAg_2(SCN)_4.2H_2O$.	I.	II.
		Found.	
Sr	15.32	15.33	....
AgSCN	58.09	57.36	....
Soluble SCN	20.29	20.42	20.52
H_2O	6.30	....	....

The Calcium Salt, $Ca(SCN)_2.2AgSCN.2H_2O$, was formed after 15 grams of silver thiocyanate had been dissolved in a concentrated solution of 50 grams of calcium thiocyanate, and also when larger quantities of the silver salt were used. Analyses of two crops were made (by Merriam):

	Calculated for $CaAg_2(SCN)_4.2H_2O$.	I.	II.
		Found.	
Ca	7.63	7.96	....
AgSCN	63.36	61.72	61.79
Soluble SCN	22.14	22.72	22.63
H_2O	6.87	....	....

XII. Caesium-Thallous Thiocyanate, $CsTl_4(SCN)_5$.

By H. L. Wells.

In attempting to prepare a caesium-thallous-barium triple salt, this compound (I.) was obtained by cooling a very con-centrated solution containing about 5 grams of thallous thio-

cyanate, 23 grams of barium thiocyanate and 8 grams of caesium thiocyanate. Another crop (II.) was prepared by adding 1 gram of thallous thiocyanate and 7 grams of caesium thiocyanate to the mother-liquor, dissolving by heating, diluting considerably and cooling. The compound forms very small fern-like growths of crystals, which apparently branch at right angles. It has a faint yellow color upon drying, and it is stable in the air. The product is entirely different in appearance from the thin scales of thallous thiocyanate which separate upon cooling hot aqueous solutions of that salt. The results of the analyses are as follows:

	Calculated for CsSCN.4TlSCN.	I.	Found. II.
Cs	10.73	11.09	10.22
Tl	65.86	62.69	65.28
SCN	23.41	24.10	23.14
Ba	....	1.63	0.40

It is to be noticed that crop I., formed in a very concentrated solution of a large amount of barium thiocyanate, was contaminated to a considerable extent with that salt; but if the analysis is corrected for the amount of that salt shown to be present by the barium determination, it becomes very satisfactory. In the other case, where a more dilute solution of barium thiocyanate was used, there was very little contamination. The formation of the double salt was observed in the absence of barium thiocyanate, but it was not considered necessary to analyze this product.

The analyses were made by titrating the sulphocyanogen in separate portions, then treating another sample with aqua regia, evaporating to dryness, taking up with water and a little sulphuric acid, and filtering off and weighing the barium sulphate; then concentrating the filtrate, adding a liberal amount of hydriodic acid and decolorizing with sulphurous acid, adding an equal volume of alcohol, cooling, filtering the thallous iodide on a Gooch filter and washing it with dilute alcohol; then evaporating the filtrate to dryness to remove hydriodic acid, precipitating the caesium as caesium platinic chloride in the presence of dilute alcohol and hydrochloric acid, and weighing the precipitate on a Gooch filter.

XIII. Caesium-Silver-Barium Thiocyanate, $Cs_3BaAg_2(SCN)_7$.

By O. G. Hupfel and H. L. Wells.

This triple salt was first prepared accidentally under conditions which are not accurately known (analysis I., by Hupfel). Four solutions were then made up hot, containing the following quantities of the salts:

	No. 1. Grams.	No. 2. Grams.	No. 3. Grams.	No. 4. Grams.
CsSCN	50	40	20	10
Ba(SCN)$_2$.3H$_2$O	10	20	40	50
AgSCN	8	8	8	8

Upon cooling and standing, after proper concentration, all these solutions gave the same triple salt in massive groups of colorless crystals in parallel position. Analysis II. was from No. 1, III. was from No. 4. Upon recrystallizing these products from small amounts of hot water very large, transparent crystals were obtained, which were usually not compound. The crystals are tetragonal, with steep pyramids, resembling the mineral apophyllite, and such magnificent and perfect crystals as these are seldom seen. The substance is perfectly stable upon exposure to the air, but it is readily decomposed by water.

After the above experiments had been made, silver thiocyanate was added to Nos. 1 and 4, eight grams at a time, in order to see if any other triple salt could be produced, but after each addition, up to the point of practical saturation, when 40 grams altogether of the silver salt had been added in each case, the same triple salt was formed. In the course of these experiments it became necessary to add 10 grams more of caesium thiocyanate to No. 4, because the double salt $BaAg_2(SCN)_4.2H_2O$ began to be deposited. The double salt CsSCN.AgSCN was finally formed in No. 1. The analyses are as follows:

	Calculated for $Cs_3BaAg_2(SCN)_7$.	I.	Found. II.	III.
Cs	34.44	....	33.30	33.78
Ba	11.86	11.35	11.75	12.86
AgSCN	28.66	28.50	28.22	27.45
Soluble SCN	25.04	25.02	25.06	25.25

Several other crops were identified by sulphocyanogen determinations, but it seems unnecessary to give these results. The analytical methods used here were the same as those which have been mentioned in connection with the double salts; hence they need not be described in this place.

A determination of the solubility of the compound in water was made by analyzing the mother-liquor after recrystallizing the salt three times. The liquid, which was perfectly clear, had stood in contact with the crystals for several days at the laboratory temperature, and had been frequently agitated. Two determinations gave 12.0 and 11.96 per cent. of SCN, corresponding to 48.0 and 47.8 per cent. of the salt. The temperature of saturation was about 19°. At this temperature, therefore, 100 parts of water dissolve about 92 parts of the triple salt.

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XIV. Caesium-Cuprous-Barium Thiocyanate, $Cs_3BaCu_2(SCN)_7$.

By H. L. Wells.

In investigating this salt the following solutions were prepared, hot and concentrated, and allowed to cool:

	No. 1. Grams.	No. 2. Grams.	No. 3. Grams.	No. 4. Grams.
CsSCN	50	40	20	10
$Ba(SCN)_2.3H_2O$	10	20	40	50
CuSCN	5	5	5	5

This amount of cuprous thiocyanate is nearly the limit of the solubility of this substance in these solutions, as it is far less soluble in solutions of soluble thiocyanates than the silver salt. From No. 1 the previously described double salt, CsSCN.CuSCN, was deposited, containing only a trace of barium; but from Nos. 2, 3 and 4 the triple salt sought was deposited (analyses I., II., and III.). The crystalline habit varied considerably in the three crops, for No. 2 gave mostly large single crystals with prominent pyramidal faces, No. 3 gave large masses of compound crystals which were exactly like the compound crystals of the silver salt, while No. 4 gave very stout, square prisms with only small pyramidal truncations. The analyses are as follows:

	Calculated for Cs₃BaCu₂(SCN)₇	I.	Found. II.	III.
Cs	37.30	....	....	....
Ba	12.85	12.25	13.27	....
CuSCN	22.74	23.89	22.30	22.55
Soluble SCN	27.11	26.32	27.32	27.27

The salt forms colorless, transparent crystals which are similar in all respects to the corresponding silver salt. It cannot be recrystallized from water, however, on account of the sparing solubility of cuprous thiocyanate in solutions of the other salts. It is stable in the air, and readily decomposed by water.

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XV. Caesium-Silver-Strontium and Caesium-Cuprous-Strontium Thiocyanates.

By H. F. Merriam.

These salts, $Cs_3SrAg_2(SCN)_7$ and $Cs_3SrCu_2(SCN)_7$, closely resemble the barium salts in every respect, so that a description of their physical properties may be omitted.

The silver salt was prepared from solutions containing the following quantities of the constituent salts :

	I. Grams.	II. Grams.	III. Grams.
CsSCN	45	30	10
Sr(SCN)₂.3H₂O	23	30	50
AgSCN	15	15	15

It was also prepared by recrystallization from a small quantity of water. The following analyses were made :

	Calculated for Cs₃SrAg₂(SCN)₇	I.	Found. II.	III.
Cs	35.99	....	....	....
Sr	7.90	8.14	....	....
AgSCN	29.95	29.41	....	....
Soluble SCN	26.16	26.24	26.15	26.25

The cuprous salt was prepared by dissolving 5 grams of cuprous thiocyanate in a saturated solution of 30 grams of caesium thiocyanate and 30 grams of strontium thiocyanate. Two crops gave the following analyses :

	Calculated for $Cs_2SrCu_2(SCN)_7$.	Found. I.	II.
Cs	39.12	....	....
Sr	8.59	8.72	....
CuSCN	23.85	24.17	....
Soluble SCN	28.44	28.53	28.48

XVI. The Caesium-Silver-Calcium, and the Caesium-Silver-Magnesium Thiocyanates.

By H. F. Merriam.

These two triple salts, $Cs_2CaAg_2(SCN)_6.2H_2O$ and $Cs_2MgAg_2(SCN)_6.2H_2O$, are capable of being recrystallized from water. They both form colorless, transparent crystals, those of the calcium salt being very large, while those of the magnesium compound are very small. The magnesium salt is evidently considerably less soluble in water and in the saline solutions than is the calcium salt, while the latter apparently has about the same degree of solubility as the previously described strontium and barium salts containing caesium and silver. It is not known whether the analogous salts under consideration are isomorphous or not.

The calcium compound was deposited by cooling and allowing to stand concentrated solutions containing the following mixtures :

	I. Grams.	II. Grams.	III. Grams.
CsSCN	50	30	20
$Ca(SCN)_2.4H_2O$	20	30	50
AgSCN	45	15	25

Another crop, IV, was prepared by recrystallization from a small quantity of water. The analyses are as follows:

	Calculated for $Cs_2CaAg_2(SCN)_6.2H_2O$.	I.	II.	Found. III.	IV.
Cs	29.36	....	....	....	....
Ca	4.43	4.61	4.58	....	....
AgSCN	36.64	35.80	36.21	35.97	....
Soluble SCN	25.60	25.90	25.70	25.95	25.59
H_2O	3.97	....	....	....	....

The magnesium salt was deposited from a solution containing 38 grams of caesium thiocyanate, 21 grams of magnesium

thiocyanate, and 15 grams of silver thiocyanate. Two crops were analyzed as follows:

	Calculated for $Cs_2MgAg_2(SCN)_6.2H_2O$.	Found.	
		I.	II.
Cs	29.87	....	....
Mg	2.74	2.87	....
AgSCN	37.29	37.17	....
Soluble SCN	26.06	26.09	26.04
H_2O	4.04	....	....

In the case of the magnesium compound no search was made for other triple salts that the same thiocyanates might form.

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XVII. Caesium-Silver-Manganous Thiocyanate, $Cs_2MnAg_2(SCN)_6.2H_2O$.

By C. S. Leavenworth and H. L. Wells.

A sample of this salt (I.) was prepared by dissolving 20 grams of the salt $Cs_4Mn(SCN)_6$ and 7 grams (two molecular proportions) of silver thiocyanate in a little hot water and cooling. Another crop (II.) was obtained by recrystallizing the first sample from a small quantity of hot water. The results of the analyses (I. by Leavenworth, and II. by Wells) are as follows:

	Calculated for $Cs_2MnAg_2(SCN)_6.2H_2O$.	Found.	
		I.	II.
Cs	28.88	28.06	28.94
Mn	5.97	6.15	....
AgSCN	36.05	35.94	36.20
Soluble SCN	25.19	25.15	25.10
H_2O	3.91	....	....

The salt forms very slender needles, having a faint greenish tint, which are stable in the air. Like the magnesium salt, it is rather sparingly soluble.

No search was made for other triple salts in this case, for the work with the analogous calcium salt, where only one was found, made the existence of others here seem improbable, and the results with the triple salts of zinc had not yet been obtained when this investigation was carried out.

XVIII. The Caesium-Silver-Nickel and the Caesium-Cuprous-Nickel Thiocyanates.

By R. T. Roberts and H. L. Wells.

These two salts, $Cs_2NiAg_2(SCN)_6.2H_2O$ and $Cs_2NiCu_2(SCN)_6.2H_2O$, are analogous in composition to the calcium, magnesium, and manganese salts, containing caesium and silver, which have been described already, but they are less soluble in water than the other salts, just referred to, so that it is impossible to make clear solutions from them with water alone when the attempt is made to recrystallize them. They form very small crystals which are stable in the air. The silver salt is sapphire-blue, while the cuprous compound is greenish-blue.

The silver salt was prepared by dissolving about 15 grams of silver thiocyanate and 75 grams of caesium thiocyanate in a solution containing 17 grams of nickel thiocyanate by boiling down to a small volume, then filtering hot and cooling. Two crops at different degrees of dilution were obtained from this solution, and the following analyses were made (I. and III. by Roberts, II. by Wells):

	Calculated for $Cs_2NiAg_2(SCN)_6.2H_2O$.	I.	Found. II.	III.
Cs	28.75	28.46	29.81	....
Ni	6.37	6.51	....	6.55
AgSCN	35.89	36.56	35.24	36.76
Soluble SCN,	25.09	24.89	24.92	25.00
H_2O	3.90	....	....	....

The cuprous salt was prepared similarly to the silver salt, but even less cuprous thiocyanate can be dissolved in solutions of the other thiocyanates than is the case with the silver compound. Two crops gave the following results (by Roberts):

	Calculated for $Cs_2NiCu_2(SCN)_6.2H_2O$.	Found. I.	II.
Cs	31.82	....	....
Ni	7.02	6.78	6.77
CuSCN	29.09	29.00	29.21
Soluble SCN	27.76	27.97	27.99
H_2O	4.31	....	....

In regard to the analyses of these salts it may be mentioned that complete decomposition by water required long heating, particularly in the case of the silver salt, and that the nickel was determined by electrolysis.

XIX. The Caesium-Silver-Zinc Thiocyanates.

By H. L. Wells.

It is very remarkable that while barium, strontium, and calcium, and apparently also magnesium, manganese, and nickel form only one triple thiocyanate with caesium and silver, zinc forms four of these salts. Another curious circumstance is the fact that all of these zinc salts are different in type from any others that we have prepared. The salts to be described are:

$$CsZnAg(SCN)_4.H_2O,$$
$$Cs_2ZnAg(SCN)_5,$$
$$CsZn_2Ag_3(SCN)_8,$$

and
$$CsZn_2Ag_4(SCN)_9.$$
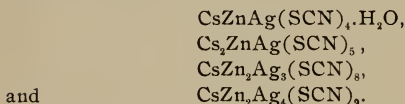
The investigation of these compounds has been very laborious, because two or three of them crystallized in various habits and were not easy to recognize by their appearance, because several of the salts are very sparingly soluble in the saline solutions, so that it was difficult to obtain crops of them of sufficient size for satisfactory analyses, and because in some cases mixtures were frequently deposited in the place of pure crops. However, it is believed that the work has been thoroughly and accurately carried out, that there is no possibility that any salt described has a variable composition or is a mixture, and that there is little probability that any other triple salts can be produced from these three thiocyanates. Large quantities of caesium and zinc thiocyanates have been employed, mixed in widely varying proportions and diluted to various degrees. The work has been done with as many as eight different solutions of these two salts, and experiments have been carried on with them continuously for several months. The amount of silver thiocyanate used was small, for this compound is very sparingly soluble in solutions containing

zinc thiocyanate, because the triple salts, as well as the double salt $ZnAg_2(SCN)_4$, dissolve in them with great difficulty. The usual method of attempting to prepare a triple salt, therefore, was to add to a caesium and zinc thiocyanate solution somewhat more of the silver salt than it would dissolve upon boiling, and to filter while hot. Sometimes a satisfactory product came down upon cooling, but if the product was not suitable for analysis, or if it was a salt which had been sufficiently investigated, it was removed, or dissolved by heating, and the solution was either allowed to stand for a few days at the ordinary temperature, or a new degree of dilution was tried.

The salt $CsZnAg(SCN)_4.H_2O$ is formed in rather concentrated solutions containing not too small an amount of zinc thiocyanate as compared with the caesium salt present. For instance, it was formed from a solution containing about 11 grams of caesium thiocyanate, 43 grams of zinc thiocyanate, and 1.25 grams of silver thiocyanate in a volume of about 100 cc., and also when the liquid was considerably diluted. It was obtained also from a solution of 23 grams of caesium thiocyanate, 11 grams of zinc thiocyanate, and an unknown, small quantity of silver thiocyanate, as well as from a solution intermediate in composition as compared with the two that have been described. The salt is deposited after the solution has cooled, upon standing, generally in small quantity. It usually forms rather slender, flattened crystals having the outline of very acute rhombs, but in several cases much broader rhomb-shaped crystals were observed. The edges of the crystals are somewhat irregular, apparently because they are formed of smaller individuals joined together. The groups are generally not as much as a centimeter in length, and only about one or two millimeters in width where the more slender habit occurs. The crystals are colorless and brilliant before being removed from the liquid, but this salt differs from all the others in losing water upon exposure to the air, thereby becoming opaque and very brittle. The following analyses, each of which represents an entirely distinct crop, were made with samples that had lost their water more

or less completely by being air-dried, or which, in two cases (V. and VI.), had been dried at 100°:

	Calculated for CsZnAg(SCN)$_4$.	I.	II.	III.	Found. IV.	V.	VI.	VII.
Cs	24.70	....	....	....	24.34	....	....	....
Zn	12.15	12.29	....	....	12.38	....	....	....
AgSCN	30.82	28.94	29.97	29.68	29.22	28.44	29.68	29.99
Soluble SCN	32.33	31.93	32.71	33.04	32.50	33.47	32.42	32.60

Water was determined in a sample of V. after it had been well dried, but before it had lost its transparency.

	Calculated for CsZnAg(SCN)$_4$.H$_2$O.	Found.
H$_2$O	3.24	2.67

The salt Cs$_2$ZnAg(SCN)$_5$ is very easily obtained from solutions which contain an excess of caesium thiocyanate as compared with the zinc salt, and which are rather concentrated. It was deposited from a solution containing 46 grams of caesium thiocyanate, 5.4 grams of zinc thiocyanate, and 2.5 grams of silver thiocyanate in a volume of about 125 cc.; also from a solution with 138 grams of caesium thiocyanate, 21.5 grams of zinc thiocyanate, and small quantities of silver thiocyanate at various degrees of dilution up to 900 cc. It usually crystallizes after a solution has become cold, and is very characteristic in its appearance, since it forms very slender, white needles of rectangular section which usually radiate from points in large numbers. A length of 5 cm. or more was observed with these needles, but their diameter is usually less than a millimeter. The needles dry well when pressed between filter-papers, and they are stable in the air. The following analyses were made of entirely distinct crops:

	Calculated for Cs$_2$ZnAg(SCN)$_5$.	I.	Found. II.	III.	IV.
Cs	36.46	37.62	....	....	....
Zn	8.97	8.70	....	8.86	....
AgSCN	22.76	22.44	22.33	22.37	22.49
Soluble SCN	31.81	31.33	30.89	31.58	31.67

The salt CsZn$_2$Ag$_3$(SCN)$_8$ is formed in solutions of caesium and zinc thiocyanates when they are saturated when hot with silver thiocyanate and cooled, or upon standing at the ordinary temperature when the solutions are too dilute to yield the

two salts that have been described. It apparently makes little difference whether the caesium thiocyanate is in large excess or not. It was formed, for instance, upon cooling a solution containing 138 grams of caesium thiocyanate and 21.5 grams of zinc thiocyanate, which had been saturated hot with silver thiocyanate at a volume of 750 cc., and it was formed in the same solution, upon standing at the ordinary temperature, when the volume was 1200 cc. It was formed also, by standing at ordinary temperature in a solution containing 17 grams of caesium thiocyanate, 16 grams of zinc thiocyanate, and a small quantity of silver thiocyanate in a volume of about 400 cc. The formation of the salt was observed also in many other cases under a wide range of conditions, but usually in quantities too small for analysis. The compound crystallizes most frequently in small, thin, colorless scales which usually have a rhombic (diamond-shaped) or rhomboidal outline. The scales seldom have a diameter as great as 5 mm. Compound crystals of considerably different habit were also observed. The substance is stable upon exposure to the air, and is slowly decomposed by cold water, but more rapidly by hot. The following analyses were made with separate crops:

	Calculated for $CsZn_2Ag_3(SCN)_8$.	I.	II.	III.	IV.	V.	VI.
Cs	12.65	....	11.79	....	....	....	13.63
Zn	12.43	12.26	....	11.91	12.01	....	....
AgSCN	47.35	47.10	47.39	46.34	43.84	....	44.06
Soluble SCN	27.57	27.65	27.35	27.53	27.95	27.18	28.47

It is believed that the determination of silver thiocyanate in IV. is erroneous, but the sample was not large enough to allow the determination to be repeated. Analysis VI. also shows considerable variations, although it was made from a very well crystallized and apparently homogeneous crop. The latter was deposited, by long standing, from a solution containing a much greater proportion of zinc thiocyanate than any of the others, *viz.*, 11.5 grams of caesium thiocyanate, 43.4 grams of zinc thiocyanate, and a small, unknown quantity of silver thiocyanate, at a volume of about 300 cc. It seems probable that this sample was contaminated with a little of the salt $CsZnAg(SCN)_4.H_2O$.

The salt $CsZn_2Ag_4(SCN)_9$ has been the cause of much perplexity during this investigation. It was the first well-crystallized triple salt of zinc encountered, and at that time two good crops of it which had been prepared from a solution of a composition not accurately known, were analyzed. When attempts were made afterwards to produce it from solutions containing known quantities of the salts it was not obtained for a long time. Finally, since it was known that the caesium thiocyanate used in the first experiments was contaminated with a considerable amount of ammonium thiocyanate, the latter salt was added to some of the experimental solutions, and from one of these, but not until after many trials, the much-sought salt was produced. It may be possible to prepare this compound in the absence of the ammonium salt, but although it has been found to contain no ammonia, this has not yet been done. A solution from which two crops were obtained at 700 and 800 cc. contained about 92 grams of caesium thiocyanate, 5.5 grams of zinc thiocyanate, 20 grams of ammonium thiocyanate, and small, unknown quantities of silver thiocyanate. The compound is deposited from cold solutions on standing. It forms very brilliant, flattened, colorless crystals, usually less than 1 cm. in length or diameter, which vary greatly in habit, although the individuals of any single crop are usually nearly uniform. The outlines of the crystals may be nearly triangular, almost square, nearly rhombic, or elongated and nearly rectangular. These variations are evidently due to the fact that the crystals are usually built up of smaller individuals which unite in various ways, apparently by twinning. The salt is stable in the air and is slowly decomposed by water. The following analyses represent four crops of crystals:

	Calculated for $CsZn_2Ag_4(SCN)_9$.	I.	II.	III.	IV.
			Found.		
Cs	10.92	....	11.55	....	....
Zn	10.74	10.75	11.44	10.29	10.46
AgSCN	54.53	53.52	54.23	53.88	54.29
Soluble SCN	23.81	23.63	23.21	24.07	23.86

In regard to the analyses of the caesium-zinc-silver salts it may be mentioned that it was found best to boil the water

added to the samples for about half an hour in order to de-
compose them completely. Soluble SCN was usually deter-
mined, without filtration, in a separate sample. Silver thio-
cyanate was weighed in a Gooch crucible, and where caesium
was not to be determined, the zinc was precipitated from the
filtrate with sodium carbonate and weighed as the oxide, also
in a Gooch crucible. When caesium was to be determined,
the zinc was first precipitated as the sulphide, then the cae-
sium was finally determined, sometimes as the normal sul-
phate and in other cases in the form of the platinum salt.

XX. POTASSIUM-SILVER-BARIUM THIOCYANATE.

BY H. L. WELLS.

This salt, $K_4BaAg_2(SCN)_8.H_2O$, was first formed by evap-
orating over sulphuric acid a solution of about 135 grams of
barium thiocyanate, 95 grams of potassium thiocyanate, and 115
grams of silver thiocyanate in a little water. The selection
of these quantities of salts was to some extent accidental, but
a very good crop of brilliant crystals was obtained forming a
coherent layer upon the surface of the dish in which the evap-
oration took place. The mother-liquor was extremely dense
and syrupy, so that it was very difficult to remove it from the
crystals by pressing them upon filter-paper, but as the crys-
tals were hard and solid, and stable in the air, this was satis-
factorily accomplished (Analysis I.). The mother-liquor
was warmed and again placed over sulphuric acid, when in a
few days a small number of small crystals began to grow.
These were taken out when they had reached a diameter of
about 1 cm. and carefully dried with paper (Analysis II. was
made from several of these crystals, III. from a single one).
When the second mother-liquor was agitated in removing the
large crystals, a very large quantity of small crystals was
rapidly formed. These were drained by suction, pressed on
paper, and then recrystallized by dissolving in water with the
aid of heat, filtering, and evaporating over sulphuric acid.
An excellent crop of rather small, transparent crystals was thus
obtained (Analysis IV.). All the crystals of this salt, which
were inspected, were in the form of rectangular pyramids

truncated with rather large, square basal planes. Mr. J. C. Blake has kindly examined the crystals and finds that the pyramidal faces do not correspond to those of the caesium-silver-barium salt, being much less steep. As has been previously mentioned the crystals are brilliant, transparent, and stable in the air. They are exceedingly soluble in small quantities of water, but are decomposed by much of it with precipitation of silver thiocyanate. The analyses are as follows :

	Calculated for $K_4BaAg_6(SCN)_8.H_2O.$	I.	II.	Found. III.	IV.	
K	15.79	....	....	....	14.78	14.73
Ba	13.85	14.55	15.15	....	14.69	14.71
AgSCN	33.47	33.27	33.19	33.24	33.17	
Soluble SCN	35.08	35.94	34.85	34.95	34.94	
H_2O	1.81	....	....	....	....	

New Haven, Conn., July, 1902.

THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE PRODUCED BY CERTAIN SALTS AND ACIDS.

By Harry C. Jones and Charles G. Carroll.

A short investigation on the lowering of the freezing-point of aqueous hydrogen dioxide by certain salts has already been carried out in this laboratory.[1] The object of the investigation was to ascertain, if possible, whether hydrogen dioxide has a greater dissociating power than water. This was all the more desirable since Calvert[2] had shown that the dielectric constant of aqueous hydrogen dioxide is greater than that of pure water; and from the Thomson-Nernst hypothesis we must conclude that the solvent with the higher dielectric constant has the greater dissociating power. The attempt was made to measure the dissociation of salts in aqueous hydrogen dioxide by means of the conductivity method, but this was abandoned on account of the decomposition of the dioxide by the metal electrodes. Bredig and Calvert[3] have since pointed out that iron covered with tin can

[1] Jones, Barnes and Hyde: This Journal, **27**, 22 (1902).
[2] Ann. der Phys., **1**, 483.
[3] Ztschr. Elektrochem., **7**, 622; Ztschr. phys. Chem, **38**, 513.

be used as electrodes for measuring the conductivity of solutions of electrolytes in aqueous hydrogen dioxide. This part of the problem has been left to them since we have learned privately from Bredig that he desires to continue work upon this phase of the subject.

The freezing-point method was resorted to as the best means available for measuring the dissociation of electrolytes in aqueous hydrogen dioxide, and Jones, Barnes, and Hyde[1] measured the freezing-point lowering of aqueous hydrogen dioxide produced by potassium chloride, sodium nitrate, and potassium nitrate. They found that the lowering of the freezing-point of aqueous hydrogen dioxide produced by the above-named salts was always less, and in the case of potassium nitrate very much less than the lowering of the freezing-point of pure water. The natural inference from these results would be that aqueous hydrogen dioxide has less dissociating power than pure water, that the presence of the hydrogen dioxide drives back the dissociation of the salt. · The lowering of the freezing-point of aqueous hydrogen dioxide is, however, so much less than that of pure water, especially in the case of potassium nitrate, that it would be very difficult to explain the results simply on the assumption of a driving back of the dissociation.

Just before the earlier work in this laboratory was published a paper appeared by Bredig,[2] and one a little later by Calvert,[3] which seemed to furnish us with a rational explanation of the results which we had obtained. Bredig and Calvert made it very probable by the conductivity, freezing-point, and other methods, that the strong alkalies can combine with hydrogen dioxide, forming definite compounds with it. They concluded that hydrogen dioxide is a weak acid.

It seemed probable from our earlier results that salts also can combine with hydrogen dioxide, especially salts like potassium nitrate.

Salts.

The present investigation was undertaken for the purpose

[1] This JOURNAL, **27**, 22 (1902).
[2] Ztschr. Elektrochem., **7**, 622.
[3] Ztschr. phys. Chem., **38**, 513.

of obtaining more data bearing on this point. Some of the earlier measurements with potassium chloride were repeated, and especially those with potassium nitrate, which gave an unexpectedly small lowering of the freezing-point of aqueous hydrogen dioxide. Hydrogen dioxide of two different concentrations was used with potassium nitrate, as will be seen from the following results.

Both of the above-named salts are binary electrolytes, yielding only two ions. It was desirable to study the lowering of the freezing-point of aqueous hydrogen dioxide, as compared with water, which would be produced by a ternary salt. Ammonium sulphate was chosen on account of its high solubility.

The hydrogen dioxide which was used was purified and concentrated by the method already described,[1] and the solutions were prepared by the same general method as that employed in the first investigation. We were especially careful to keep the temperature low while the salt was dissolving in the dioxide, and in every case we determined the concentration of the dioxide after the salt had completely dissolved. In most cases the amount of decomposition was so slight that it could be neglected. Wherever an appreciable decomposition had taken place a corresponding correction in the freezing-point of the pure solvent was introduced.

The strength of the hydrogen dioxide, both before and after the solution of the salt, was determined by titrating with a solution of potassium permanganate of known concentration.

The results which were obtained with the three salts named above are given in the following tables. The first column contains the strength of the solution of the salt, the second the lowering of the freezing-point of the aqueous hydrogen dioxide corrected for the separation of ice. The third is the molecular lowering of the freezing-point of the dioxide. The strength of the dioxide employed is given in percentage.

For the sake of comparison the lowerings of the freezing-point of water produced by the same substances at the same concentrations were determined under exactly the same con-

[1] This JOURNAL, **27**, 24 (1902).

ditions as the lowering of the freezing-point of the dioxide. The results for aqueous solutions are also given below:

Potassium Chloride in Water.

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$3°.370$	$3°.370$
0.75	$2°.521$	$3°.362$
0.50	$1°.6745$	$3°.349$
0.25	$0°.838$	$3°.341$
0.20	.....	$3°.430$
0.10	.....	$3°.469$

Potassium Chloride in Hydrogen Dioxide (4.35 per cent).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$2°.996$	$2°.996$
0.50	$1°.465$	$2°.930$
0.25	$0°.719$	$2°.876$
0.125	$0°.3555$	$2°.844$
0.0625	$0°.182$	$2°.944$
0.03125	$0°.094$	$3°.008$

Potassium Nitrate in Water.[1]

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$2°.656$	$2°.656$
0.75	$2°.107$	$2°.809$
0.50	$1°.470$	$2°.940$
0.25	$0°.771$	$3°.084$

Potassium Nitrate in Hydrogen Dioxide (4.35 per cent).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$2°.264$	$2°.264$
0.50	$1°.245$	$2°.490$
0.25	$0°.651$	$2°.604$
0.125	$0°.342$	$2°.736$

Potassium Nitrate in Hydrogen Dioxide (5.507 per cent).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$2°.156$	$2°.156$
0.50	$1°.193$	$2°.386$
0.25	$0°.613$	$2°.452$
0.125	$0°.320$	$2°.560$

[1] Jones, Barnes, and Hyde: This JOURNAL, **27**, 29.

Ammonium Sulphate in Water.

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$3°.761$	$3°.761$
0.50	$1°.934$	$3°.868$
0.25	$1°.026$	$4°.104$
0.20[1]	. . . . .	$4°.145$
0.10[1]	. . . . .	$4°.370$

Ammonium Sulphate in Hydrogen Dioxide (4.108 per cent).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$3°.203$	$3°.203$
0.50	$1°.634$	$3°.268$
0.25	$0°.8545$	$3°.428$
0.125	$0°.445$	$3°.560$
0.0625	$0°.233$	$3°.728$

Ammonium Sulphate in Hydrogen Dioxide (3.23 per cent).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.00	$3°.203$	$3°.203$
0.50	$1°.665$	$3°.330$
0.25	$0°.871$	$3°.484$
0.125	$0°.454$	$3°.632$
0.0625	$0°.237$	$3°.792$

A comparison of the above results with those obtained by Jones, Barnes, and Hyde, will show that the former confirm the latter. The lowering of the freezing-point of aqueous hydrogen dioxide by potassium chloride is much less than the lowering of the freezing-point of water produced by the same salt at the same concentrations.

The measurements of the freezing-point lowerings produced by potassium nitrate were repeated with special care, using two concentrations of the dioxide. This seemed desirable on account of the very small values found in the first investigation with this salt. Our results confirm very satisfactorily those of Jones, Barnes, and Hyde.

The conclusion which applies to the above two salts holds also for ammonium sulphate. The lowering of the freezing-point of the dioxide is much less than that of water under the same conditions of concentration of the salt.

The relations between the lowering of the freezing-point of

[1] Jones: This Journal, 19, 115.

H_2SO_4 in aqueous H_2O_2 4·876 %

H_2SO_4 in H_2O

$C_2H_2O_4$ in aqueous H_2O_2 3·836 %

$C_2H_2O_4$ in H_2O

Molecular Lowering

Concentration

$(NH_4)_2SO_4$ in H_2O

KCl in H_2O

$(NH_4)_2SO_4$ in aqueous H_2O_2 4·108 %

KCl in aqueous H_2O_2 4·35 %

KNO_3 in H_2O

KNO_3 in aqueous H_2O_2 4·35 %

KNO_3 in aqueous H_2O_2 5·507 %

Molecular Lowering
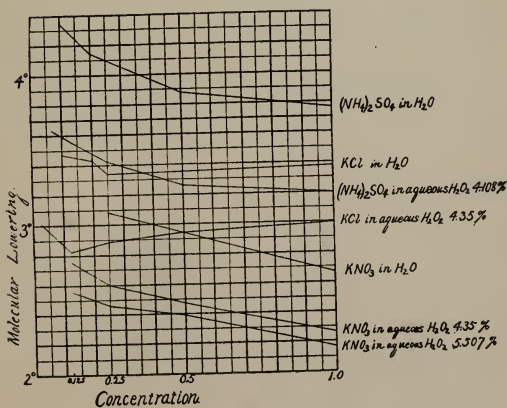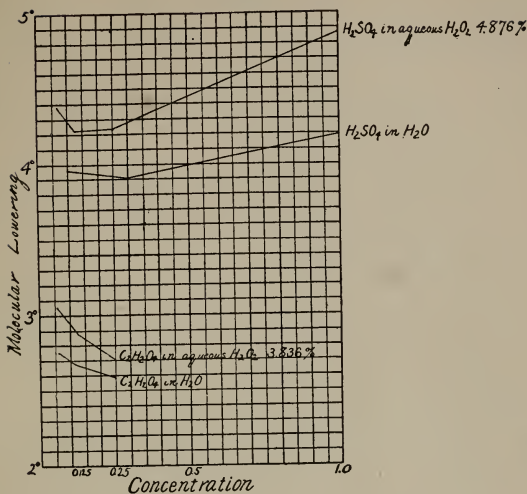
Concentration

water and of the aqueous solution of the dioxide, as produced by the above-named salts, can be seen best by plotting the two sets of values for each salt in the form of curves. The abscissas are concentrations of the salt in the solvent, the ordinates are molecular lowerings of the freezing-point. The curves for water as the solvent, lie, in every case, well above those in the aqueous dioxide.

From results similar to these Bredig and Calvert concluded that the strong alkalies form compounds with aqueous hydrogen dioxide or, in other words, that hydrogen dioxide in the presence of water is a weak acid.

Our results with the above-named salts can apparently be interpreted in several ways. The dioxide may effect great polymerization of the salt molecules, or may greatly drive back the dissociation of the salt. Both of these explanations seem to us improbable, especially when we consider the results obtained with potassium nitrate. The lowering of the freezing-point of aqueous hydrogen dioxide produced by this salt is so much less than the lowering of the freezing-point of water, that it is difficult to account for the difference on the assumption either of polymerization or a driving back of the dissociation.

The most probable explanation of the above results, all things considered, seems to us to be that there is union between the molecules of the several salts investigated and the molecules of hydrogen dioxide. This is made the more probable by the work of Tanatar,[1] who pointed out the existence of compounds of potassium fluoride and hydrogen dioxide, and also of sodium sulphate and sodium nitrate and the dioxide.

Acids.

Having found the above results with salts we next turned our attention to acids, to see whether relations similar to the above existed between the freezing-point lowering of water and of aqueous hydrogen dioxide, produced by them. This was all the more desirable since Bredig and Calvert had already worked with bases and had discovered relations similar to those found by us for salts.

[1] Ztschr. anorg. Chem., **28**, 255.

The work carried out thus far with acids is only preliminary. We, however, give the results which we have obtained:

Sulphuric Acid in Water.

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.0	$4°.190$	$4°.190$
0.5	$2°.030$	$4°.060$
0.3	$1°.173$	$3°.910$
0.1	$0°.396$	$3°.960$

Sulphuric Acid in Aqueous Hydrogen Dioxide (*4.876 per cent*).

Concentration.	Observed F. P. lowering.	Molecular lowering.
1.0	$4°.859$	$4°.859$
0.5	$2°.220$	$4°.440$
0.25	$1°.056$	$4°.244$
0.125	$0°.528$	$4°.224$
0.0625	$0°.274$	$4°.384$

Oxalic Acid in Water.

Concentration.	Observed F. P. lowering.	Molecular lowering.
0.25	$0°.646$	$2°.576$
0.125	$0°.336$	$2°.688$
0.0625	$0°.1725$	$2°.760$

Oxalic Acid in Aqueous Hydrogen Dioxide (*3°.836 per cent*).

Concentration.	Observed F. P. lowering.	Molecular lowering.
0.25	$0°.680$	$2°.720$
0.125	$0°.360$	$2°.880$
0.0625	$0°.204$	$3°.264$

The results for acids are plotted as curves (Fig. II.), which show clearly that the lowering of the freezing-point of aqueous hydrogen dioxide is considerably greater than that of water. These results would indicate that the acids are dissociated to a greater extent by the dioxide than by water. The data thus far obtained for acids are, however, so meager that no final conclusion can be drawn from them. We propose to repeat the above measurements as well as extend this investigation to a much larger number of substances.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June, 1902.

III.—ON THE AROMATIC GUANIDINES.

By Frederick J. Alway and Frederick W. Viele.

Marckwald[1] has carefully investigated the action of aniline, of *p*-toluidine, and of *o*-toluidine upon diphenylcarbodiimide, and that of aniline and of *o*-toluidine upon di-*o*-tolylcarbodiimide, and less carefully the action of some of these aromatic amines upon mixed carbodiimides such as phenyl-*p*-tolylcarbodiimide, as well as their action upon some of the corresponding thioureas of the general formulæ :

$$\begin{array}{c} \diagup NHR \\ C{=}S \\ \diagdown NHR \end{array} \qquad \text{and} \qquad \begin{array}{c} \diagup NHR \\ C{=}S \\ \diagdown NHR' \end{array}.$$
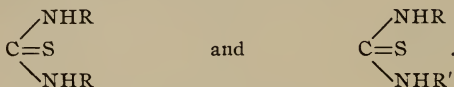
He found that pentaphenyldiguanide,

$$\begin{array}{c} C_6H_5.NH{-}C{-}N{-}C{-}NH.C_6H_5 \\ \diagup\!\!\diagup \quad | \quad \diagdown\!\!\diagdown \\ C_6H_5.N \quad C_6H_5 \quad N.C_6H_5 \end{array},$$
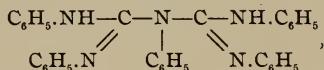
was formed, together with triphenylguanidine, by allowing an alcoholic solution of aniline and diphenylcarbodiimide to stand for a time at the temperature of the room. A great excess of aniline did not prevent the formation of the diguanide. The analogous tetraphenyl-*p*-tolyldiguanide and diphenyl-*p*-tolylguanidine were obtained by the action of *p*-toluidine upon diphenylcarbodiimide. The formation of this diguanide was not proven in the preparation of the guanidine from aniline and phenyl-*p*-tolylcarbodiimide, from *p*-toluidine and diphenylthiourea with lead oxide, or from aniline and phenyl-*p*-tolylthiourea with lead oxide. *o*-Toluidine, unlike aniline and *p*-toluidine, did not react with diphenylcarbodiimide to produce a diguanide as well as a guanidine. Diphenyl-*o*-tolylguanidine was the only product of the reaction. The reaction followed a different course where *o*-tolyl groups were present.

Both phenyldi-*o*-tolylguanidine and tri-*o*-tolylguanidine

[1] Ann. Chem. (Liebig), **286**, 361.

were formed by the interaction of di-*o*-tolylcarbodiimide and aniline, of phenyl-*o*-tolylcarbodiimide and *o*-toluidine, of di-*o*-tolylthiourea, aniline, and lead oxide, and of phenyl-*o*-tolyl-thiourea, *o*-toluidine, and lead oxide. The tri-*o*-tolylguani-dine was the only compound obtained by the action of *o*-tolu-idine upon di-*o*-tolylcarbodiimide.

In the hope of finding some relation between the course of the reaction and the structure of the reacting diimide or that of the amine, we have undertaken a thorough investigation of the formation of diguanides and guanidines of the general formulæ :

$$\begin{array}{c} R^4NH \\ R^5N \end{array}\!\!\!>\!\! C\!-\!N\!-\!C\!\!<\!\!\begin{array}{c} NHR^2 \\ NR^1 \end{array} \quad \text{and} \quad C\!\!=\!\!NR^2 \!\!<\!\!\begin{array}{c} NHR^1 \\ \\ NHR^3 \end{array},$$
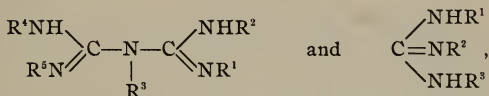
wherein R^1, R^2, R^3, R^4, and R^5 are all alike, partly alike, or all different.

As this investigation must be discontinued for some time we give below the results of our work up to the present time. *m*-Toluidine is analogous to *p*-toluidine in its action upon di-phenylcarbodiimide, yielding a mixture of diphenyl-*m*-tolyl-guanidine and tetraphenyl-*m*-tolyldiguanide, or the former of these compounds alone, according to the conditions under which the reaction is allowed to take place.

EXPERIMENTAL.

Pentaphenyldiguanide, $\quad \begin{array}{c} C_6H_5.NH \\ C_6H_5.N \end{array}\!\!\!>\!\! C\!-\!N\!-\!C\!\!<\!\!\begin{array}{c} NH.C_6H_5 \\ N.C_6H_5 \end{array}$.—
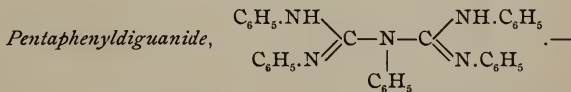
That we might form some idea of the yield of this compound under favorable circumstances, we prepared it according to the method described by Marckwald,[1] as he had kindly in-formed us in a private communication that he had no record of the yield of the guanidines and the diguanides described in his article to which we refer.

Twelve grams diphenylcarbodiimide (boiling-point 192° at 28 mm.) and 3 grams freshly distilled aniline were mixed to-

[1] *Loc. cit.*

gether with 40 cc. alcohol (90 per cent). After standing a few days at the temperature of the room the mixture had become an almost solid mass. The white, crystalline mass thus obtained was extracted with 330 cc. of warm alcohol (90 per cent) and washed on the filter several times with hot alcohol of the same strength. The dried residue weighed 8 grams. The product thus obtained melted at 157°. (Triphenylguanidine melts at 144° and pentaphenyldiguanide at 160°.) The same compound was obtained by melting 11 grams β-diphenylcarbodiimide and adding to this liquid 3 grams aniline. The mixture solidified on cooling to a transparent, glassy mass. After standing for two months it had undergone no change in appearance. It was then melted. The molten substance, on being stirred, changed to a white, crystalline mass. This was treated with 90 per cent alcohol in the same manner as the product obtained in the preceding experiment. The residue in this case weighed only 1.5 grams. The insoluble substance thus obtained was fully identified as pentaphenyldiguanide.

Tetraphenyl-p-tolyldiguanide,

$$\begin{matrix} C_6H_5.NH \\ \diagdown \\ C_6H_5.N \diagup \end{matrix} C-N-C \begin{matrix} NH.C_6H_5 \\ \diagup \\ \diagdown N.C_6H_5 \end{matrix}$$
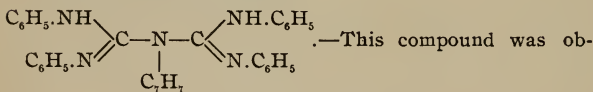
with C_7H_7 below the central N.—This compound was obtained by dissolving 7 grams diphenylcarbodiimide and 3.5 grams *p*-toluidine in absolute alcohol and allowing the mixture to stand at the temperature of the room. The crystalline mass, after treatment with excess of boiling 90 per cent alcohol, yielded 1.25 grams of the above compound. This compound seems to be formed in smaller quantity by the action of *p*-toluidine (1 mol.) and lead hydroxide upon diphenylthiourea (1 mol.) in alcoholic solution. An excess of *p*-toluidine does not prevent its formation. When the reaction-product is extracted with 95 per cent alcohol, even the tenth extract gives a white deposit on cooling. This substance was found to be diphenyl-*p*-tolylguanidine and evidently results from the gradual decomposition of the diguanide.

Tetraphenyl-m-tolyldiguanide,
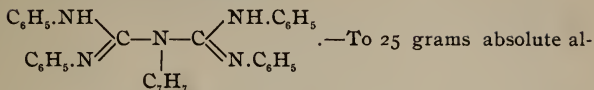
$$\begin{array}{c} C_6H_5.NH \\ \\ C_6H_5.N \end{array}\!\!\!\!>\!\!C\!-\!N\!-\!C\!<\!\!\!\begin{array}{c} NH.C_6H_5 \\ \\ N.C_6H_5 \end{array}$$.—To 25 grams absolute al-

cohol we added 5.1 grams *m*-toluidine and 10 grams diphenyl-
carbodiimide. Within five minutes the temperature had risen
20° to 30°. After four hours a white solid began to separate
out. The mixture was stirred frequently during the follow-
ing ten hours, and at the end of a day and a half was an al-
most solid, white, crystalline mass. This was warmed with
90 per cent alcohol and repeatedly washed on the filter with
boiling alcohol of the same strength. The filtrate contained
diphenyl-*m*-tolylguanidine. The white residue weighed 8
grams and melted at 136°. The melting-point was not sharp.
Recrystallization from absolute alcohol, from benzene, or solu-
tion in benzene and precipitation from this by ligroin did not
give a substance with a higher melting-point. The residue
consists of pure tetraphenyl-*m*-tolyldiguanide. The base is
readily soluble in acetone and benzene, much less soluble in
boiling absolute alcohol, and only sparingly soluble in ether,
ligroin, cold absolute alcohol, or boiling aqueous alcohol.

	Calculated for $C_{33}H_{29}N_5$.	Found.
N	14.1	14.0

The hydrochloride was obtained by covering the finely pul-
verized base with warm alcohol and adding to this mixture
an excess of concentrated hydrochloric acid. The clear solu-
tion thus obtained was placed in a freezing-mixture of ice and
salt and, while kept agitated, an excess of ice-cold water was
added in small portions. A white, crystalline precipitate
was formed. This was thoroughly washed on the filter with
ice-cold water.

	Calculated for $C_{33}H_{29}N_5$.HCl.	I.	II.	III.
HCl	6.9	6.4	6.8	6.5

By the addition of a dilute aqueous solution of platinic chlo-
ride to the solution of the above chloride in dilute alcohol, the
chlorplatinate was obtained as a flesh-colored, amorphous pre-

cipitate, which melted at 140° with decomposition. It is readily soluble in alcohol, but insoluble in water.

	Calculated for $(C_{33}H_{29}N_5)_2H_2PtCl_6$.	Found.
Pt	13.9	13.9

Diphenyl-m-tolylguanidine, $C \begin{smallmatrix} \diagup NH.C_6H_5 \\ = N.C_7H_7 \\ \diagdown N.H.C_6H_5 \end{smallmatrix}$.—This compound
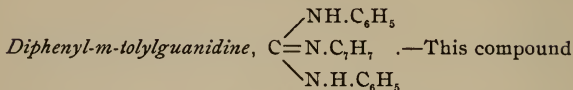
was obtained, together with the diguanide described above, by the action of *m*-toluidine (1 mol.) upon diphenylcarbodiimide (2 mol.) in the cold. It was the chief product when *p*-toluidine (1 mol.) was mixed with diphenylcarbodiimide (1 mol.) in absolute alcohol, and the mixture allowed to stand at the temperature of the room for several days. At the end of this time a small amount of the diguanide (0.25 gram) had separated out and was removed by filtration. When the mixture (of 1 mol. with 1 mol.) was heated on the water-bath for two hours, no diguanide was obtained, the whole reaction-product being readily soluble in hot, 90 per cent alcohol. Some impurity is, however, present in all the above cases, as the guanidine separated out of the solution very slowly, and in varying amounts, as colorless crystals, which did not possess a sharp melting-point, while the pure guanidine crystallizes readily from aqueous alcohol.

The following was found to be the most satisfactory method of obtaining it in quantity. Diphenylthiourea (1 mol.) was dissolved in the minimum amount of boiling ordinary alcohol, *m*-toluidine (1 mol.) added, and lead hydroxide then added in small portions until the desulphurization was complete. The hot reaction-mixture was filtered under suction and the black residue of lead sulphide boiled with a quantity of alcohol equal to that used in the first case, and the mixture filtered. The two alcoholic solutions were mixed, cooled under the tap, and treated with a quantity of concentrated nitric acid slightly greater than the theoretical amount required. The solution became red and crystals soon began to separate out. After some hours had elapsed the crystals were filtered out, washed with a little cold alcohol, redissolved in this sol-

vent, and boiled with bone-black. On cooling the filtered solution colorless crystals were obtained. After the fourth recrystallization from alcohol the melting-point remained constant at 179°. The base was obtained from the nitrate by treatment with dilute potash, and recrystallization from alcohol. This compound crystallizes in stellate groups of colorless needles that melt at 132°. It is very soluble in hot absolute alcohol and in hot benzene, from both of which it crystallizes on cooling. It is soluble in aqueous alcohol and in ether, but insoluble in water.

	Calculated for $C_{20}H_{19}N_3$.	Found.
N	13.9	14.0

The *nitrate* is readily obtained by the addition of nitric acid to the alcoholic solution of the base. It forms colorless, hard crystals, which melt with decomposition at 179°, and are readily soluble in hot alcohol, and sparingly soluble in cold alcohol and in water.

	Calculated for $C_{20}H_{19}N_3.HNO_3$.	I.	Found. II.	III.
HNO_3	17.3	17.6	17.8	17.6

The *hydrochloride* was obtained by treating the alcoholic solution of the base with dilute hydrochloric acid. It forms colorless plates that melt at 195°. It is slightly soluble in cold water, and readily soluble in cold alcohol.

	Calculated for $C_{20}H_{19}N_3.HCl$.	I.	Found. II.
HCl	10.8	11.2	11.2

The *chlorplatinate* is obtained by the addition of platinic chloride to the solution of the hydrochloride in aqueous alcohol. It forms orange-red leaflets that melt at 237°.

	Calculated for $(C_{20}H_{19}N_3)_2H_2PtCl_6$.	Found.
Pt	19.2	19.4

UNIVERSITY PLACE,
May, 1902.

THE DETERMINATION OF PHOSPHORIC ACID BY MEANS OF AMMONIUM PHOSPHOMOLYBDATE.

By Gregory Paul Baxter.

The composition of ammonium phosphomolybdate has received considerable attention with a view to its use, when weighed directly, as a means of determining phosphoric acid. But although it has been shown that under definite conditions the precipitate has, within certain limits, a fixed composition, the effect of varying conditions has never been carefully studied, and the consensus of opinion has been that its composition is too uncertain to warrant its use for the accurate estimation of phosphoric acid.

The formula usually assigned to the ammonium phosphomolybdate is $(NH_4)_3PO_4.12MoO_3$, which contains 3.783 per cent of phosphoric anhydride. That this formula is only an approximation can be seen from the following experimental results:

> Rammelsberg[1]—Dried at 100°   3.90
> Finkener[2]—Washed with ammonium nitrate and heated to volatilization of the nitrate   3.794
> Gladding[3]—Washed with 1 per cent nitric acid and dried at 105°   3.76

Furthermore, the after treatment of the precipitate is not the only factor which determines its composition. Few substances are so susceptible to the influence of the conditions under which precipitation takes place. Hence it is not at all surprising that the method under discussion has never found favor in the eyes of quantitative analysts.

Most methods of determining phosphoric acid in the presence of bases precipitable by ammonia require preliminary precipitation of the phosphoric acid by molybdic acid. Solution of the ammonium phosphomolybdate in ammonia and double precipitation of the magnesium ammonium phosphate

[1] Ber. d. chem. Ges., 10, 1776.
[2] Ibid., 11, 1638.
[3] J. Am. Chem. Soc., 18, 23.

is troublesome and time-exacting, and, since much manipulation is necessary, correspondingly inexact. Pemberton's volumetric method of solution in standard potassium hydroxide and titration with standard acid is subject to the errors due to loss of ammonia even when $N/5$ solutions are used, and to the uncertainty of the end-point with phenolphthalein in the presence of ammonium salts. The method of weighing the ammonium phosphomolybdate has two great advantages. First, the precipitate can be washed and collected with great ease on account of its granular nature ; and secondly, a high ratio exists between its weight and the weight of its phosphoric acid content, for the weight of the phosphomolybdate is between eight and nine times as great as that of an equivalent amount of magnesium ammonium phosphate. Thus a very considerable error in the weight of the phosphomolybdate would influence but slightly the accuracy with which the phosphoric acid could be determined.

The following research was the result of a conviction that it was possible so to regulate the conditions which determine the composition of the phosphomolybdate as to make it possible to obtain a substance of constant composition.

The first step in the problem was to prepare the precipitate in a state suitable for weighing. For this purpose a washing solution was necessary, in which the precipitate is insoluble, and which subsequently can be completely removed from it. Water decomposes the precipitate, as is well known ; nitric acid dissolves it ;[1] molybdic acid cannot be removed without washing with some other medium. Ammonium nitrate, on the other hand, neither decomposes nor dissolves the precipitate,[2] and it can be completely volatilized at a comparatively low temperature. Evidently, if the precipitate could be heated to the point at which ammonium nitrate decomposes, no better medium for washing could be obtained than a solution of this salt. Such proved to be the case. The phosphomolybdate, when washed with a 10 per cent solution of ammonium ni-

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[1] About a gram of the precipitate was digested for some time with 1 per cent nitric acid in the cold. The solution, after filtration and evaporation, left a residue. Stronger acid gave a yellow solution. See also Eggertz : J. prakt. Chem., **79**, 496.

[2] Stankel found the yellow precipitate to be least soluble in neutral ammonium nitrate. Ztschr. anal. Chem., **21**, 353.

trate, can be heated to constant weight at 300° without decomposition. Since ammonium nitrate is converted into nitrous oxide and water at 220°±,[1] the decomposition of this salt must be complete at 300°. This is evident from the following experiments.

A solution of calcium phosphate in nitric acid was added to an excess of the ordinary molybdic acid solution,[2] both solutions being at the room temperature. After being thoroughly washed by decantation with 10 per cent ammonium nitrate, the precipitates were collected in porcelain Gooch crucibles. The crucibles with the precipitates were heated in a small copper air-bath, 12 cm. in diameter and 13 cm. in height, and jacketed with one thickness of heavy asbestos paper. With such a bath a temperature of 300° is obtainable by means of a good Bunsen burner. Copper oxidizes rapidly at the above temperature, and the bath becomes coated both inside and out with scales of copper oxide, which are easily detached,—a source of contamination of the precipitate unless great care is exercised. A porcelain air-bath is exempt from the above disadvantages, but, on the other hand, is very liable to breakage at the high temperature employed, as well as being much less easily heated to the desired temperature. Where electricity is available an electric air-bath of either glass or porcelain affords a superior means of heating the precipitate. The precipitates were cooled in desiccators containing sulphuric acid, for it was found that they gradually gained in weight in the desiccator when fused calcium chloride was used as a drying agent.[3]

At temperatures below 290° the precipitates lost in weight so slowly that the attempt to obtain constant weight was given up. At 290° the weight became constant within a little more than a milligram in 3 grams, after three hours' heating, while at 300° this result was reached even more quickly. Where saving of time is an object the latter temperature is preferable. However, care must be exercised that the temperature does not much exceed 300°, since decomposition of the pre-

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[1] Dammer : Handbuch der anorg. Chem., II., **2,** 272.

[2] Made by dissolving 150 grams of ammonium molybdate in 1 liter of water and pouring the solution into 1 liter of nitric acid of the sp. gr. 1.2.

[3] The fact that the precipitate is very hygroscopic was noted by Finkener. Ber. d. chem. Ges., **11,** 1638.

cipitate, accompanied by blackening and loss of weight, sets in.   Up to 325° the precipitate retains its yellow color which is considerably darker at high temperatures than the lemon-yellow color which it possesses when cold.[1]

Table I.

Period of each heating.	Temperature. Centigrade.	Weight of precipitate I.	Weight of precipitate II.	Weight of precipitate III.	Weight of precipitate IV.	Weight of precipitate V.	Weight of precipitate VI.
Hrs.		Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
3	290°	2.8952	2.8968	....	....	....	....
18	290°	2.8945	2.8955	....	....	....	....
18	290°	....	....	2.8942	2.8946	....	....
18	290°	....	....	2.8935	2.8938	....	....
1	300°	....	....	....	....	2.9107	2.9149
2	300°	....	....	....	....	2.9097	2.9149
18	290°	....	....	....	....	2.9092	2.9144

A standard solution of phosphoric acid was prepared as follows : Disodium phosphate was purified by five recrystallizations, in platinum vessels, with water which had been condensed in a block-tin condenser.   About 25 grams of the crystals were dissolved in 500 cc. of water.   As soon as possible after the solution had been prepared, it was analyzed, first by evaporation of weighed portions of the solution in platinum crucibles and ignition of the residue, then by precipitation of the phosphoric acid by slowly dropping magnesia mixture into fresh portions of the solution after each had been diluted to a volume of 75 cc.   The agreement of the results obtained by the two methods leaves no doubt as to the strength of the solution.

Table II.

Number of analysis.	Weight of solution. Grams.	Weight of $Na_4P_2O_7$. Gram.	Weight of $Mg_2P_2O_7$. Gram.	Per cent P_2O_5.
1	25.262	0.4358	....	0.9202
2	39.808	0.6867	....	0.9202
3	40.550	0.6991	....	0.9197
			Average,	0.9200
4	25.436	....	0.3669	0.9197
5	30.499	....	0.4400	0.9198
			Average,	0.9198

[1] Eggertz also found that at 325° the precipitate is still yellow. J. prakt. Chem., **79**, 496.

The first experiments with the ammonium phosphomolybdate were carried out by precipitation of the phosphoric acid in the above solution by means of the solution of molybdic acid generally recommended for the purpose (see foot-note, page 300). Weighed portions of about 10 cc. of the phosphate were diluted to 50 cc. (*i. e.* so that the solution contained about 1 decigram of phosphoric anhydride in 50 cc.), and were then added to about 100 cc. of the molybdic acid solution. Both solutions were at the room temperature. Obviously this method is better than pouring the molybdic acid into the phosphate, for the mechanical inclusion of molybdic acid solution would have far less effect upon the weight of the precipitate than the inclusion of the phosphoric acid. As a matter of fact, several experiments carried out in the reverse manner yielded anomalous results which have not yet been investigated. The liquid was immediately colored yellow, although precipitation began in most cases only after several seconds and proceeded slowly. As would be expected, precipitation was hastened by stirring, and in fact, incomplete precipitation resulted in some cases where vigorous stirring was omitted. Within an hour in the cold the precipitate had settled in great part, leaving a solution which was still colored slightly yellow and which continued to deposit a precipitate for several hours longer. After standing at least sixteen hours the precipitates were washed with 10 per cent ammonium nitrate and collected in weighed porcelain Gooch crucibles. This operation is easily carried out, for although the precipitate adheres to the sides of the containing vessel to a considerable extent it can be easily detached by friction, best with a rubber ''policeman.'' The granular nature of the precipitate aids very materially in the washing and transferring. The precipitates were finally heated for eighteen hours at 290° before being weighed.

The ammonium nitrate was found to be free from chloride and sulphate by the usual tests. Furthermore, 10 cc. of the washing solution were evaporated to dryness in a platinum crucible and the residue then heated to 290° in the air-bath. The crucible gained 0.0002 gram, hence the nitrate must have been essentially free from alkalies also.

Table III.

Number of analysis.	Weight of solution. Grams.	Weight of P_2O_5 calculated.[1] Gram.	Molybdic acid. cc.	Weight of precipitate. Grams.	Per cent of P_2O_5 in precipitate.
6	10.0895	0.09282	100	2.4803	3.7425
7	10.1076	0.09299	100	2.4842	3.7432
8	10.1571	0.09344	100	2.4982	3.7404
9	10.1240	0.09314	100	2.4880	3.7436
10	10.1975	0.09382	90	2.5088	3.7396
11	10.1050	0.09297	90	2.4864	3.7389
12	10.1350	0.09324	80	2.4902	3.7453
13	10.1340	0.09323	80	2.4894	3.7443

Average, 3.7422

In Analysis 12, 0.5 cc., and in Analysis 13, 1 cc. of concentrated nitric acid was added to the phosphate before precipitation. Evidently such slight changes in the conditions as those indicated produce no appreciable effect.

Since the formula $(NH_4)_3PO_4.12MoO_3$ demands 3.783 per cent of phosphoric anhydride, this formula cannot represent the composition of the precipitate obtained as above. The cause of the discrepancy could be determined only by analyzing the precipitate.

New solutions of phosphoric acid, of such a strength that 25 cc. contained very nearly 1 decigram of phosphoric anhydride, were now prepared by dissolving calcium phosphate in nitric acid. Portions of 25 cc. were precipitated with molybdic acid under exactly the same conditions as before. From the weights of the precipitates so obtained were calculated the strengths of the solutions, assuming the percentage of phosphoric anhydride to be 3.742. Since in no case did the weights of the precipitates obtained from the same solution vary more than 0.1 per cent, this method must afford an accurate estimation of the phosphoric acid.

A number of the precipitates were then analyzed for ammonia as follows: The precipitate was transferred from the crucible to a retort by means of a stream of water from a wash-bottle, an operation easily accomplished since the precipitate showed no tendency to adhere to the crucible. To the tubu-

[1] In calculating the weight of phosphoric anhydride the result obtained by evaporation of the solution was used.

lature of the retort was fitted a separating-funnel which served to introduce a strong solution of sodium hydroxide without danger of loss of ammonia. The ammonia was then determined by distillation into N/5 hydrochloric acid in the usual way.

Table IV.

Number of analysis.	Weight of precipitate. Grams.	Weight of $(NH_4)_2O$. Gram.	Per cent of $(NH_4)_2O$.
14	2.8916	0.1161	4.016
15	2.8938	0.1164	4.022
16	2.4937	0.1006	4.034

Average, 4.024

Since it was possible that the precipitate contained water as well as molybdenum trioxide, the water was determined by combustion of the total hydrogen in several samples. From the weight of water found was subtracted that corresponding to 4.024 per cent of ammonium oxide.

Table V.

Number of analysis	Weight of precipitate. Grams.	Weight of water. Gram.	Weight of water equivalent to 4.024 per cent $(NH_4)_2O$. Gram.	Difference. Gram.	Per cent of water.
17	2.0668	0.1169	0.1149	0.0020	0.097
18	2.2310	0.1259	0.1241	0.0018	0.074
19	2.9017	0.1639	0.1613	0.0026	0.090
20	3.4095	0.1915	0.1896	0.0019	0.056

Average, 0.079

The sum of phosphoric acid, ammonia, and water is 7.843 per cent. The remainder, 92.16 per cent, can be due to molybdic acid only. Below are tabulated the results obtained experimentally and those calculated from the formula $(NH_4)_3PO_4.12MoO_3$.

	Calculated for $(NH_4)_3PO_4.12MoO_3$.	Found.
P_2O_5	3.783	3.742
$(NH_4)_2O$	4.167	4.024
MoO_3	92.06	92.16
H_2O	....	0.079

To explain the discrepancy between the experimental and theoretical percentages of phosphoric anhydride by assuming other stoichiometric relations between phosphoric anhydride and molybdenum trioxide in the precipitate, would lead to an extremely complicated and impossible formula. Such an assumption is, however, unnecessary. The solution from which precipitation takes place contains a large excess of the precipitant, hence nothing is more probable than that the precipitate carries down molybdic acid in excess of the theoretical quantity. If we allow 24 MoO_3 for each P_2O_5, there are required by 3.742 per cent of the latter 91.08 per cent of the former, while the corresponding percentage of ammonia is 4.123. The extent of the occlusion, 1.08 per cent, is by no means an impossible quantity. The low experimental result for ammonia is probably due to loss of ammonia by the precipitate at the high temperature to which it was subjected, or perhaps even at ordinary temperature while in contact with the strongly acid solution from which it was precipitated. The substitution of a hydrogen atom for an ammonium radical might be expected to have no marked effect upon the color of the compound. This explanation will also account for the presence of a portion of the water. The difference between the experimental and theoretical percentages of ammonium oxide, 0.099, is equivalent to 0.034 per cent of water, nearly one-half the total quantity found. The remainder may be easily accounted for by the well-known difficulty of obtaining a "blank" determination of water in combustion, and by the possibility that even at 300° the precipitate retained a trace of moisture.

Quite recently T. W. Richards has shown that the carrying down of foreign substances by precipitates is not mechanical inclusion of these substances but rather the result of a law of distribution of the portion of these substances existing in an electrically neutral condition, between the solution and the precipitate at the moment of formation. Obviously, he points out, any change in the substances present in solution which tends to diminish the concentration of the group under consideration, tends to diminish the amount occluded. This has been found to hold true in the cases of the occlusion of iron

and chromium salts by barium sulphate[1] and of magnesium oxalate by calcium oxalate.[2]

In the present case we can represent the equilibria in the solution by the following scheme :

$$
\begin{array}{c}
2NH_4NO_3 \\
\uparrow\downarrow \\
2HNO_3 \rightleftharpoons 2NO_3^- + 2H^+ \\
+ \qquad\qquad + \\
2NH_4^+ + MoO_4^= \rightleftharpoons (NH_4)_2MoO_4 \\
\uparrow\downarrow \\
H_2MoO_4
\end{array}
$$
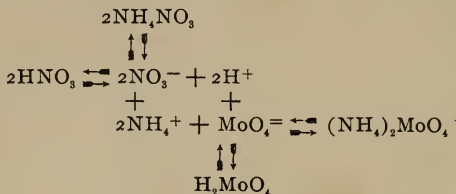
If, then, the occlusion is due to undissociated molybdic acid, an increase in the concentration of either the hydrogen or the molybdic ion should produce an increase in the extent of the occlusion ; while, if ammonium molybdate is the primary cause, an increase in the concentration of either the ammonium or the molybdic ion or a decrease in the concentration of the ionized hydrogen should result in increased weight of the precipitate.

One hundred cc. of molybdic acid solution is more than double the amount theoretically necessary to combine with 1 decigram of phosphoric anhydride. It has been shown already (Table III.) that small variations in the quantity used produce no appreciable effect upon the weight of the phosphomolybdate. If 50 cc. are used, *i. e.*, a slight excess, precipitation is incomplete. Filtration was carried out after twenty-four hours, but the filtrate deposited a large amount of precipitate as soon as the ammonium nitrate of the washing solution was mixed with it. After standing twenty-four hours longer, the filtrate and wash-waters were filtered, and again a further addition of ammonium nitrate produced a precipitate.

Seventy-five cc. of precipitant also were found insufficient to produce complete precipitation, but the filtrate was completely freed from phosphoric acid by the ammonium nitrate of the washing solution. In this experiment (Analysis 21)

[1] Proc. Am. Acad., **35**, 377.
[2] *Ibid.*, **36**, 377.

the first filtration yielded 2.8568 grams, the second 0.0387 gram of precipitate. In another case (Analysis 22) 100 cc. of 10 per cent ammonium nitrate were added some time after precipitation. Complete precipitation was the result, as also in Analyses 23 and 24, where the same amount of ammonium nitrate was added to the molybdic acid before precipitation.

Table VI.

No. of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per ceut P_2O_5.	Weight of $(NH_4)_2O$. Gram.	Per cent of $(NH_4)_2O$.
21	100	2.8955	0.1083	3.740	....	....
22	100	2.8928	0.1083	3.743	0.1171	4.049
23	100	2.9004	0.1086	3.744	....	....
24	100	2.9026	0.1086	3.742	....	....
			Average,	3.742		

In these experiments the effect of ammonium nitrate in decreasing the solubility of the precipitate is marked, but from the fact that the composition of the precipitate is essentially identical with that obtained in Table IV., and is the same whether the ammonium nitrate is added before or after the precipitate is formed, it is evident that it had little influence upon the occlusion. This is to be expected, for the molybdic acid solution itself contained a large amount of ammonium salt (about 60 grams of ammonium nitrate in a liter).

In the following table are given the results obtained by the use of larger quantities of molybdic acid. Naturally no difficulty was experienced through incomplete precipitation :

Table VII.

No. of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent P_2O_5.	Weight of $(NH_4)_2O$. Gram.	Per cent $(NH_4)_2O$.
25	200	2.9046	0.1083	3.728	0.1189	4.093
26	200	2.9044	0.1083	3.728	....	....
27	200	2.9049	0.1083	3.728	....	....
28	200	2.9042	0.1083	3.729	....	....
			Average,	3.728		
29	300	2.9409	0.1094	3.721		

These results support the foregoing hypothesis of co-pre-cipitation in a striking manner. If the water content of these precipitates be neglected, the percentage of molybdenum tri-oxide is in both cases very nearly 92.18. Since 3.728 and 3.721 per cent of phosphoric anhydride correspond to 90.73 and 90.56 per cent of molybdenum trioxide, respectively, the occlusion in the two cases amounts to 1.4 and 1.6 per cent. Evidently occlusion increases with the concentration of the molybdate but at a much slower rate. Each decigram of phosphoric anhydride requires theoretically about 35 cc. of molybdic acid solution, hence an excess of 160 cc. of molyb-dic acid gives a precipitate containing 3.728 per cent of phos-phoric anhydride. If the excess of molybdic acid is 260 cc. the percentage is 3.721, while with an excess of from 50 to 70 cc. it is 3.742 (Table III). Here are sufficient data for com-puting the percentage of phosphoric anhydride in any pre-cipitate formed under the conditions which have been con-sidered. The curve given on page 314 embraces all points corresponding to an excess of between 60 and 260 cc. of molybdic acid.

It has been shown that the chief effect of ammonium nitrate is to diminish the solubility of the precipitate. Although in Analyses 21 to 24 no influence was exerted on the composi-tion of the precipitate by ammonium nitrate, it was interest-ing to determine its effect in the presence of more molybdic acid. In Analyses 30 to 33, 100 cc. of a 10 per cent solution of ammonium nitrate were added to the molybdic acid solution before precipitation, and in Analyses 34 to 39, 10 grams of the salt were dissolved in each 100 cc. of the molybdic acid. The differences between these results and those in Table IV. are of negligible magnitude. In the presence of larger quantities of molybdic acid, however, the effect of ammonium nitrate on the composition of the precipitate becomes more marked. In Analyses 40 and 41, 10 grams of ammonium nitrate were dis-solved in the molybdic acid, in Analyses 42 and 43, 100 cc. of 20 per cent ammonium nitrate solution were added. Hence the results are comparable with those of Table VII., where the conditions were exactly the same except that the ammo-nium nitrate was omitted. The difference in the percentage

of phosphoric anhydride, though slight (—0.005 per cent), is large enough to show conclusively that the occlusion increases with the concentration of the ionized ammonium.

Table VIII.

No. of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent P_2O_5.	Weight of $(NH_4)_2O$. Gram.	Per cent of $(NH_4)_2O$.
30	100	2.8908	0.1083	3.746	0.1159	4.013
31	100	2.8941	0.1083	3.742	....	....
32	100	2.8954	0.1083	3.740	....	....
33	100	2.8975	0.1083	3.737	0.1166	4.024
34	100	2.8952	0.1083	3.740	....	....
35	100	2.8956	0.1083	3.740	0.1173	4.052
36	100	2.8927	0.1083	3.743	0.1182	4.085
37	100	2.8938	0.1083	3.742	....	....
38	100	2.8945	0.1083	3.741	0.1170	4.041
39	100	2.8955	0.1083	3.740	....	....
			Average,	3.741	Average,	4.043
40	200	2.9100	0.1083	3.721	....	....
41	200	2.9075	0.1083	3.724	0.1179	4.054
42	200	2.9187	0.1086	3.721	....	....
43	200	2.9142	0.1086	3.727	....	....
			Average,	3.723		

Where the excess of molybdic acid is not too large, the addition of ammonium nitrate before precipitation is a distinct advantage, for it not only hastens the reaction but also assures complete precipitation. The following experiments were carried out with molybdic acid containing 100 grams of ammonium nitrate per liter. In Analyses 46 to 48 it was found possible to reduce the period of standing to one-tenth that necessary in the absence of ammonium nitrate. The filtrate in Analysis 44 became turbid upon standing, while that in Analysis 45 was cloudy:

Table IX.

Number of analysis.	Molybdic acid. cc.	Period of standing. Minutes.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.
44	100	15	2.8946	0.1086	....
45	100	30	2.8993	0.1086	....
46	100	60	2.9014	0.1086	3.743
47	100	120	2.8991	0.1086	3.746
48	100	120	2.9019	0.1086	3.743

If ammonium molybdate is the substance occluded by the precipitate we should expect that a diminution in the concentration of the ionized hydrogen, by increasing the dissociation of the molybdic acid, would bring about an increase in this occlusion. This proved to be the case, for in Analyses 49 and 50, in which one-half the usual excess of nitric acid was present in the molybdic acid solution, the precipitates were over a centigram heavier than before. It was found impossible to study the action of larger quantities of nitric acid because an amount sufficient to be noticeable in its effect produced incomplete precipitation. For instance, in Analyses 51 and 52, 5 cc. of concentrated nitric acid were added to the molybdic acid. Here the filtrates were yellow, showing that precipitation was not even approximately complete.

Table X.

No. of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.	Weight of $(NH_4)_2O$. Gram.	Per cent of $(NH_4)_2O$.
49	100	2.9149	0.1083	3.715	0.1178	4.042
50	100	2.9097	0.1083	3.722	....	....
51	100	2.8365	0.1083	....	....	....
52	100	2.7916	0.1083	....	....	....

When a smaller amount of nitric acid and an increased amount of ammonium nitrate acted together, their combined influence was very much larger than that of either alone. In Analyses 53 to 56 the results were obtained with a molybdic acid solution containing half the usual acid and 20 grams of ammonium nitrate in each 100 cc.

Table XI.

No. of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.	Weight of $(NH_4)_2O$. Gram.	Per cent of $(NH_4)_2O$.
53	100	2.9208	0.1083	3.708	....	....
54	100	2.9202	0.1083	3.708	0.1184	4.054
55	200	2.9525	0.1083	3.668	....	....
56	200	2.9531	0.1083	3.667	0.1203	4.074

In Analysis 56 the ammonia content demanded by 3.667 per cent of phosphoric anhydride is 4.040, while that found experimentally was 4.074. The occlusion in this analysis is

at its maximum, and since the excess of ammonia could have come only from the occluded substance, here is additional proof that this substance is ammonium molybdate.

One other condition should influence the composition of the precipitate, the dilution at which precipitation takes place. In many of the foregoing experiments the molybdic acid was diluted to double its original volume with ammonium nitrate (Analyses 30, 31, 42 to 48). Here no appreciable effect was produced. In Analyses 57 and 58 the phosphate was diluted so that 1 decigram of phosphoric anhydride was contained in 100 cc. of water. Precipitation was incomplete in these cases. When diluted with 10 per cent ammonium nitrate solution to the same volume, the phosphate yielded results identical with those obtained with stronger solutions (Analyses 59 and 60). Evidently the effect of dilution, if appreciable, is neutralized by the large amount of ammonium nitrate.

Table XII.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.	Weight of P_2O_5 in filtrate calculated. Gram.
57	100	2.8569	0.1083	. . . .	0.0014
58	100	2.8566	0.1083	. . . .	0.0014
59	100	2.4810	0.09282	3.741	. . . .
60	100	2.4775	0.09273	3.743	. . . .

Since the concentration of the molybdic acid is always very large, even after precipitation is complete, and since under all conditions the formation of the precipitate is gradual, the rate at which the phosphate is added to the molybdate should have no marked effect. In Analysis 61 the phosphate was added in portions of about 1 cc., and the greater part of the precipitate from each portion was allowed to form before further addition, while in Analysis 62 the phosphate was added drop by drop from a burette. About fifteen minutes were taken for each precipitation. In order to hasten precipitation, 50 cc. of 20 per cent ammonium nitrate were added to the molybdic acid before precipitation. This has been shown already to have no appreciable effect upon the composition of the precipitate except where a large excess of molybdic acid is pres-

ent. The results of these experiments are essentially identical with those obtained by rapid addition of the phosphate.

Table XIII.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.
61	100	2.9006	0.1086	3.744
62	100	2.8992	0.1086	3.746

It was interesting to determine whether occlusion takes place wholly at the time of precipitation or while the precipitate is standing in contact with the solution from which it is precipitated. In two experiments precipitation was carried out in the presence of an excess of 60 cc. of molybdic acid and much ammonium nitrate; then, after the lapse of an hour, 100 cc. more were added and the whole allowed to stand an hour before filtration.

Table XIV.

Number of analysis.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.
63	2.9116	0.1086	3.730
64	2.9113	0.1086	3.730

Precipitation must have been complete at the end of the first hour (see Analyses 46 to 48), so that the observed decrease in the percentage of phosphoric anhydride below that when the excess of molybdic acid is 60 cc. (—0.012 per cent) must have been due to increased occlusion owing to the second addition of molybdic acid.

In all probability, then, occlusion takes place in two stages, at the time of precipitation and while the precipitate is standing in contact with the solution. The first should be dependent on the concentration of the substances in the solution at the time of precipitation; the second evidently depends upon the conditions which exist in the solution after precipitation and also upon the time during which the precipitate is allowed to stand before filtration. This is shown by the following experiments, in which the precipitates remained five days in contact with the solution.

Table XV.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Weight of P_2O_5 calculated. Gram.	Per cent of P_2O_5.
65	80	2.2709	0.0846	3.726
66	80	2.2733	0.0846	3.722
67	160	2.2938	0.0846	3.689
68	160	2.2908	0.0846	3.693

During this time the precipitates with the smaller excess of molybdic acid increased in weight 0.5 per cent, those with the larger excess, 1 per cent. Obviously, although the gain in weight per day is very small, 0.1 per cent in one case, 0.2 per cent in the other, the filtration should be carried out as soon as possible after the precipitation is complete.

The results of this investigation are as follows :

1. The precipitate formed by the addition of a solution of a phosphate to an excess of molybdic acid has the formula $(NH_4)_3PO_4.12MoO_3$.

2. The precipitate occludes ammonium molybdate at the moment of precipitation, and later absorbs more of this salt. The amount of the latter varies considerably with the concentration of the undissociated ammonium molybdate in solution and the time during which the precipitate remains in contact with the solution.

3. This occluded ammonium molybdate loses the greater part of its ammonia at 290°, so that the excess in weight of the precipitate, after it has been heated to this temperature, is due to molybdenum trioxide.

4. Under definite conditions the occlusion has a constant value. This has been determined for various conditions, so that the weight of the precipitate can be used for the estimation of phosphoric acid.

5. The conditions most favorable to exact analysis are as follows : The solution should contain about 1 decigram of phosphoric anhydride in 50 cc. If much nitric acid is present, the greater part should be removed by evaporation. The phosphate should be poured, with vigorous stirring, into a quantity of the usual molybdic acid solution at least 50 cc. in excess of the amount theoretically necessary to precipitate

the phosphoric acid, both solutions being at the room temperature. After standing about sixteen hours the precipitate should be washed with 10 per cent ammonium nitrate solution, transferred to a Gooch crucible, and heated to 300° for at least two hours. From the weight of the precipitate the excess of molybdic acid can be found by first making an approximate estimation of the phosphoric anhydride. The exact percentage of phosphoric anhydride can then be found from the following curve.

In order to hasten precipitation, ammonium nitrate may be added. Ten grams for 100 cc. of molybdic acid is sufficient to produce complete precipitation within one hour. The percentages of phosphoric anhydride in precipitates obtained in this way are only slightly different from those obtained without the use of ammonium nitrate.
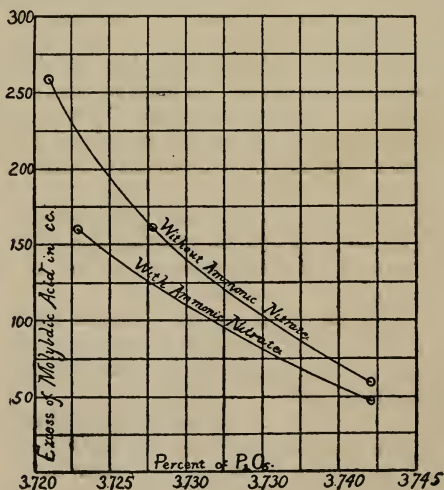
It must be clear from this paper that the accuracy and rapidity with which phosphoric acid can be determined by weighing the ammonium phosphomolybdate are such as to

entitle this method to a place among the standard analytical processes. For, by conducting the precipitation in the presence of a large amount of ammonium nitrate and heating the precipitate to 300°, results accurate within 0.1 per cent can be obtained within four hours.

CHEMICAL LABORATORY OF SWARTH-
MORE COLLEGE, SWARTHMORE, PA.,
June 23, 1902.

ON AN ACID DERIVATIVE OF ETHYL ANILINO-MALONATE.

BY RICHARD SYDNEY CURTISS.

In a former paper[1] I gave a brief description of the action of nitrous acid on ethyl anilinomalonate, by which was produced an oil possessing acid properties, to which the formula

$$\text{I.} \quad C_6H_5-N-C \underset{N}{\overset{CO_2C_2H_5}{<}} CO_2C_2H_5,$$
$$\underset{OH}{\overset{|}{N}}$$
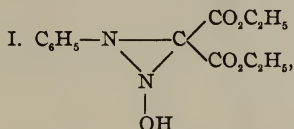
ethyl α-phenyloxydiazomalonate was tentatively given.

The substance has since been prepared in larger quantities and studies made of its potassium, sodium, and ammonium salts, and also of the effect of heat, and of acetic anhydride upon it. Reduction by zinc and acetic acid liberates nitrogen as ammonia and yields ethyl anilinomalonate,

$$C_6H_5-N-C \overset{CO_2C_2H_5}{\underset{CO_2C_2H_5}{<}}.$$
$$\quad\quad H \;\; H$$
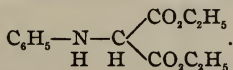
The results of tests of its electrical conductivity and the rapidity with which it forms a salt with alcoholic potash are the best indications yet found for the above constitutional formula, I., as opposed to the isomeric form:

$$\text{II.} \quad C_6H_5-N-C \overset{CO_2C_2H_5}{\underset{CO_2C_2H_5}{<}}.$$
$$\underset{NO}{\overset{|}{\quad}} H$$
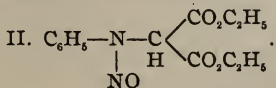
[1] This JOURNAL, **23**, 509.

(Ethyl nitrosoanilinomalonate.) The precipitation of the ammonium salt by addition of dry ammonia gas to the body, in solution in a non-ionizing solvent, is soon to be tried.[1] The body gives with ferric chloride solution a deep-red color, and does not give the Liebermann nitroso reaction.

A detailed account of the experimental work follows :

Preparation of the Acid Oil.—The following conditions, closely observed, yielded the best results : Twenty grams of finely powdered ethyl anilinomalonate, prepared by the method already described,[2] are suspended in 30 cc. of water containing 4.8 grams of sulphuric acid (theory, 4 grams). This is shaken in a glass-stoppered bottle with a solution of 5.9 grams of sodium nitrite (theory, 5.5 grams) in 50 cc. of water. The latter solution is added in small quantities, with violent shaking, while the temperature is kept at 12° to 16° by frequent immersion in ice-water. The reaction begins immediately after the addition of the nitrite. The nitrous acid is rapidly and completely absorbed, the particles of ester becoming oily. After one-half of the salt has been added, the oily mass begins to break up and to separate into a fine emulsion. After all of the nitrite has been added the shaking is continued for ten minutes, and the mass is then allowed to settle. The aqueous solution is separated in a funnel from the oil and extracted repeatedly with ether. The oil is then added to the latter and washed thoroughly with cold water, then with a little sodium carbonate solution to remove all traces of mineral acids, and lastly very thoroughly with cold water. After drying over calcium chloride the ether is distilled off in a vacuum at 0°. The product is best kept in a desiccator over sulphuric acid in a dark room.

The utmost care is requisite in carrying out the above operation, as very slight variations in the quantities of the reagents, in the temperature, or in the time consumed in the operation, as well as in the degree of washing, have a marked effect on the purity of the oil and its keeping qualities.

Thus prepared, the product is a thick, clear, amber oil, of slightly reddish tint by transmitted light, and possessing a

[1] Hantzsch and Dollfus : Ber. d. chem. Ges., **35,** 226.
[2] Curtiss : This JOURNAL, **19,** 693.

bitter taste. It is easily soluble in benzene, ether, alcohol, chloroform, and glacial acetic acid, very slightly soluble in ligroin and in water. Strong bases dissolve it easily with formation of yellow solutions. Sodium carbonate solution appears to act but slowly on it. Heat and sunlight readily decompose it with evolution of gases (oxides of nitrogen) and formation of a thick red oil. It may sometimes be kept from four to six weeks over sulphuric acid, with little change. On the other hand, the slightest traces of impurity or even neutral substances (grains of glass or sand, etc.) will decompose it quickly.

The molecular weight determinations of the oil, as well as the analyses of the sodium and potassium salts, already given,[1] show the substance to have the empirical formula $C_{13}H_{16}O_5N_2$, required for a body of the structure represented by I.

The following tests of the electrical resistance of the oil and its potassium salt were made in absolute alcohol solutions (20 cc.), using the same cell in all experiments (with dull platinized electrodes 1 cm. apart) immersed in a water-bath provided with a thermostat. The readings were made with a Wheatstone bridge and telephone arrangement, using an alternating current. The sample of oil used was freshly prepared and very carefully purified, and dried in a vacuum over sulphuric acid.

Experiment I.

Determination of the resistance of a N/10 solution of potassium hydroxide in absolute alcohol, and the rate of change of the resistance on addition (1) of 0.5 molecule of the acid oil, and (2) a second 0.5 molecule of the acid oil in N/10 solution in absolute alcohol.

[1] This JOURNAL, **23**, 510.

Temperature, 19°.

Time in minutes.	Readings on Wheatstone bridge.		Interposed resistance.	Observed resistance.	Specific resistance per cc. of solution.
	a.	b.	w.	x.	k.
	(KOH solution.)		Ohms.	Ohms.	
	501	499	90	89.6	1.1115
0	(Added 0.5 mol. acid oil, 10 cc.)				
1	530	470	230	204	0.25296
1.5	520	480	230	212	0.26326
8.5	515	485	230	217	0.2686
15.5	514	486	230	218	0.2703
17.5	(Added 2nd 0.5 mol. acid sol., 10 cc.)				
18.5	558	442	730	578	0.7170
19.5	555	445	730	585	0.7258
22.5	554	446	730	588	0.7291
23.5	554	446	730	588	0.7291
31.5	554	446	730	588	0.7291
47.5	554	446	730	588	0.7291
1 hr. 47.0	558	442	730	578	0.7170
21 hrs.[1]	690	310	730	328	0.4067

Experiment II.

Determination of resistance of a N/10 solution of the acid oil in absolute alcohol, after addition of 20 cc. of N/10 potassium hydroxide solution (1 mol.) in absolute alcohol.

Temperature, 19°.

Time in minutes.	a.	b.	w.	x.	k.
10	534	466	700	611	0.7576
15	535	465	700	608	0.7539
17 hrs.	490	510	400	420	0.5208

In this experiment quick readings could not be made directly after the addition of the alkali, owing to a defect in fixing the interposed resistance.

Experiment III.

Determination of the resistance of the absolute alcohol used in experiments I. and II.

Temperature, 19°.

a.	b.	w.	x.	k.
135	865	11000	70481	87.393

[1] Crystals have separated out in small quantity.

Experiment IV.

Determination of the resistance of a $N/3$ solution of the acid oil in the absolute alcohol used in experiment III. (1.87 gram oil in 20 cc. alcohol).

Temperature, $19°.5$.

a.	b.	w.	x.	k.
284	716	11000	27732	34.3875

The values of a and b are the mean of twelve readings taken at intervals of two minutes. No change in the resistance was noticed after the first reading, but the telephone minimum was indistinct.

Experiment V.

Determination of the resistance of the cell used in the preceding experiments. A $N/10$ aqueous solution of potassium chloride was used.

Temperature $25°$.

a.	b.	w.	x.	Cell resistance.
490	510	10	10,408	0.00124

From the above test (I.) it would appear that the oil under consideration is in large part, if not wholly, a true acid (formula I.), as it seems very improbable that a non-acid (formula II.) would change to an acid body instantaneously, or so nearly so, by addition of potassium hydroxide and subsequent splitting off of water, thus:
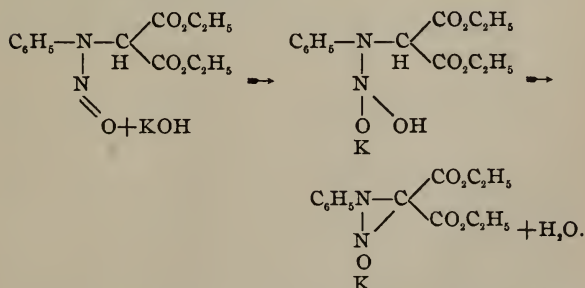
Sodium Salt.—To prepare the sodium salt of the acid oil in

its greatest purity, 18 cc. of a 10 per cent solution of sodium hydroxide (0.2 gram excess of sodium hydroxide) are added, in small portions, to 12.2 grams of the clear amber oil. The canary-yellow salt immediately separates from the oily mixture. The mass is rubbed with a glass rod until it is finely divided and entirely free from oily appearance. The temperature must be kept below 15° during the operation as the aqueous solution of the salt decomposes at ordinary temperatures. At the end of three-quarters of an hour the crystal mass is thoroughly freed from the liquid with the aid of a pump and carefully washed, first with small quantities of ice-water, next with dry ether, then with chloroform. This treatment frees the salt from all alkali and oily impurities and leaves it sufficiently pure for analysis, as the figures already given[1] show. The yield is nearly quantitative.

The sodium salt has the following properties : It forms canary-yellow needles, easily soluble in alcohol, and acetic ether, fairly soluble in ether, and water, slightly so in chloroform. An aqueous solution of the salt soon changes, (probably by hydrolysis and partial decomposition) yielding a light, clear-yellow oil of a peculiarly sweet, penetrating odor, which is unstable and decomposes in a short time, yielding colorless needles, which melt near 112°.

All attempts to recrystallize the sodium salt from solutions in the above solvents result in its partial decomposition. Slow heating, at 70° to 100°, causes the evolution of oxides of nitrogen and the formation of a yellow oil of the peculiar odor mentioned above. When quickly heated it melts at 118° to 122°.

Regeneration of the Acid Oil from Its Sodium Salt.—8.75 grams of the pure yellow salt are placed in a separatory funnel with 20 to 25 cc. each of ether and water. Dilute sulphuric acid in the slightest excess is slowly added in small portions, and the mixture well shaken, the temperature being kept below 12° to 14°. The ethereal solution is very thoroughly washed, first with a little sodium carbonate solution then many times with ice-water. The ethereal solution is

[1] *Loc. cit.*

dried over calcium chloride and the ether distilled off in a vacuum at 0°. The product is 7.1 grams of a thick oil, identical in all its properties with the original body from which the sodium salt was formed.

The Potassium Salt.—This is best made in an analogous manner and by observing the precautions referred to in the preparation of the sodium derivative. Three-tenths of a gram of potassium hydroxide (theory 0.28 gram) in solution in 2 cc. of ice-water are gradually added to 1.4 grams of the oil, the temperature being kept below 15°. After half an hour of thorough mixing the salt is filtered and washed, as above described. The product is a yellow salt which, if made in more dilute solution, separates out in fine crystal form, having the appearance of orthorhombic sulphur. It melts on quick heating at 118° to 120° with evolution of gas. It is easily soluble in water and absolute alcohol, slightly soluble in chloroform and benzene, insoluble in ligroin. (Analytical results in preliminary report.) If perfectly dry and pure this salt keeps for weeks without decomposition. It is easily decomposed, however, in aqueous solution at ordinary temperatures, more rapidly on heating, yielding apparently the same yellow oil that is formed from the sodium salt under like conditions.

The ammonium salt of the acid oil is formed when it is shaken with a slight excess of concentrated ammonium hydroxide, at low temperatures. The body precipitates out as a light-yellow salt, easily soluble in water and ether. It is much less stable than the salts of sodium and potassium. It decomposes in the desiccator over sulphuric acid, and on boiling its ethereal solution, it hydrolyzes, yielding ammonia and a clear amber oil, which possesses the properties of the original substance from which the salt is formed.

The effect of heat on the acid oil is to decompose it with evolution of gases, consisting chiefly of nitrogen and nitric oxide, with small quantities of carbon dioxide. A thick, red, neutral oil, which cannot be distilled in a vacuum, is left behind. 9.8 grams of the acid body are placed in a small flask provided with a gas-delivery tube and immersed in a paraffin-bath, the gases evolved being collected over cold water. As

the temperature of the oil is raised to 110° gas begins to be evolved. By gradually increasing the temperature for two hours, from this point to 180°, a steady and rapid flow of gas is maintained. After this time the gas ceases to come off. The contents of the flask weigh 8.5 grams and emit a pungent odor. A small quantity of water is also a product of the decomposition. On analysis, 57 cc. of the gas which escaped were found to consist of

	cc.
NO	31.5
N	22.5
CO_2	3.0
	57.0

From the residual oil in the flask a crystal mass separated on cooling. The mixture was shaken with ether and washed repeatedly with dilute sodium hydroxide solution, and lastly with water. (The alkaline wash-water, when treated with hydrochloric acid and ether, yielded 0.15 gram of a dark oil, smelling strongly of phenols.)

The yellow ethereal solution, dried over calcium chloride and distilled in a vacuum, left 7.3 grams of oil, from which 0.82 gram of needle crystals separated on cooling. This product was purified by boiling a solution of it in absolute alcohol with bone-charcoal, and recrystallizing from the same solvent. It melted constantly at 111°, giving a clear oil, which evolved gases at 200° to 250° and turned dark. The analysis gave the following figures :

0.1669 gram substance gave 18.2 cc. N gas at 19° and 741.4 mm., equivalent to 12.50 per cent.

The substance crystallizes in white, silky needles, insoluble in cold water and sodium hydroxide. It is slightly soluble in hot water and in hydrochloric acid, fairly so in alcohol and ether, easily soluble in acetone and benzene. The oily mother-liquor from the above crystal body could not be distilled in a vacuum. It was treated with aniline, and after twenty-four hours the mixture, on being rubbed up with ether and hydrochloric acid, yielded 3.5 grams of grayish-

white needles. The substance was boiled with bone-charcoal and alcohol (95 per cent). The yellowish-white crystals obtained melted (not sharply) at 110° to 111°. An attempt to further purify this body by treatment with bone-charcoal in 60 per cent alcohol resulted in its decomposition into a yellow oil, with a slight odor of aniline.

Action of Acetic Anhydride on the Acid Oil.—Four and two-tenths grams of the pure amber oil mixed with 3 grams of acetic anhydride (2 mol.) was heated in a flask provided with a reverse condenser and calcium-chloride tube, and immersed in a paraffin-bath. At a temperature of 125° to 130° gases are rapidly evolved. The color of the oil does not change within two and a half hours with rise of temperature up to 160°. At the end of three hours the operation was stopped. The contents of the flask had lost 0.8 gram in weight, and from 80 to 90 cc. of gas had been collected over water. On cooling the oil, crystals separate, and an odor of acetic ether was noticed on opening the flask, indicating the loss of an ethoxy group.

The ethereal extract of the oil was washed with a dilute solution of sodium hydroxide, and with water, and dried with calcium chloride. After removing the ether by distillation, 0.9 gram of white crystals were obtained. This product, recrystallized from absolute alcohol and washed with ether, yielded pure, silky, white needles, having a sharp melting-point, 111° to 111°.5, and giving a clear oil. This substance is neutral and is identical in properties and nitrogen content with the body formed by heating the acid oil alone (see p. 322).

Analysis:

		Found.	
	I.		II.
C	54.4		54.3
H	4.60		4.5
N	12.47		....

Analyses I. and II. are of samples from different experiments, carried out under like conditions. Two series of molecular weight determinations with this body gave:

I. *By the Boiling-point Method in Pure Benzene.*

Determinations.	S. Grams.	L. Grams.	Δ.	Molecular weight M. Found.
1	0.0506	32.39	0°.011	379
2	0.1548	"	0°.055	232
3	0.2543	"	0°.093	226

II. *By the Freezing-point Method in Pure Benzene.*

Determinations.	S. Grams.	L. Grams.	Δ.	Molecular weight. M. Found.
1	0.0807	13.07	0°.143	212
2	0.1524	"	0°.262	218

Analyses of the lower fraction of the gases evolved in the above experiment on gradually raising the temperature of the bath to 93° during one and a half hours showed : Nitrogen, about 76 to 78 per cent by volume ; nitric oxide, 20 per cent ; carbon dioxide, 2 to 3 per cent. A second fraction obtained by further heating, for two hours, at a temperature of 93° to 130°, contained : nitrogen, 40 per cent ; nitric oxide, 55 to 60 per cent ; with very little carbon dioxide.

In the first experiment in which the action of acetic anhydride upon the acid oil was tried, a neutral substance was obtained, having much the same crystalline appearance as the above-mentioned body (m. p. 111°). It was easily soluble in chloroform, ether, acetone, and benzene ; slightly so in hot water and alcohol ; insoluble in ligroin and in cold sodium hydroxide solution. A boiling solution of potassium hydroxide dissolves it slightly, with apparent saponification. It melted at 114°. A molecular weight determination[1] gave the figure 340. The theoretical for an acetyl derivative,

$$C_6H_5N\!\!-\!\!-\!\!NO.OCCH_3$$
$$C_2H_5O_2C\!-\!\overset{\displaystyle\vee}{C}\!-\!CO_2C_2H_5$$
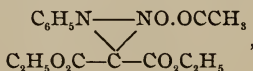
is 322.

After many attempts I have been unable to obtain enough of this body for further study and analysis.

Reduction of the Acid Oil.—One and four-tenths grams of oil

[1] This JOURNAL, **23**, 511.

in partial solution in 50 per cent acetic acid was treated with granulated zinc. The evolution of gas proceeds very slowly after a few minutes. After standing one-half hour at the room temperature the mixture was gently warmed, when the evolution of gas started again. The solution and suspended oil turned green during the process. Sufficient dilute acetic acid is added from time to time to prevent precipitation of salts, and the whole allowed to stand at the temperature of the room for eighteen hours. It is then neutralized with sodium hydroxide solution and repeatedly extracted with ether. The latter is dried over calcium chloride and distilled off on the water-bath. From the residual oil 0.7 gram of crystals separate on standing a short time. This product is purified by boiling its solution in alcohol with bone-charcoal. Evaporation of the alcohol leaves a thick, clear, light-green oil, which immediately forms a mass of monoclinic crystals on being rubbed with a glass rod (characteristic behavior of ethyl anilinomalonate). The pure body is greenish-white, melts sharply at 44°, is easily soluble in alcohol, ether, chloroform, acetone, and benzene ; fairly soluble in ligroin ; insoluble in water. It reduces cold ammoniacal silver nitrate solution, giving, when heated, a strong silver mirror. It is oxidized by mercuric oxide to ethyl dianilinomalonate,[1]

$$\begin{matrix} C_6H_5.NH \\ C_6H_5.NH \end{matrix}\!\!>\!\!C.(CO_2C_2H_5)_2.$$
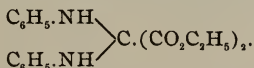
The aqueous solution in this reduction experiment, after extraction with ether, was evaporated to dryness. The salt residue, when treated with sodium hydroxide, gave proof of the presence of large quantities of ammonium salts. This, together with the formation of ethyl anilinomalonate, indicates that in the reduction of the acid oil with zinc and acetic acid the nitrogen of the isonitroso (or nitroso) group is split off in the form of ammonia.

Reduction experiments were also tried with 2.5 per cent sodium amalgam, working in neutral, acid, and alkaline solutions, in the hope of forming an intermediate reduction body

[1] This JOURNAL, **19**, 694.

containing both nitrogen atoms, possibly a three-membered ring compound

$$C_6H_5-N \underset{NH}{\overset{|}{\diagdown}} C \diagdown^{COOR}_{COOR},$$
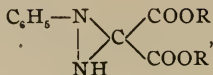
or a β-substituted phenylhydrazine derivative,

$$C_6H_5-N-\underset{\underset{NH_2}{|}}{C}\diagdown^{COOR}_{H}{}_{COOR}.$$
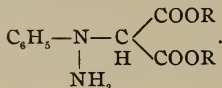
In one case 0.4 gram of a yellow crystalline body was obtained, which was soluble in acids, sodium hydroxide, and water.

In all the cases of reduction studied, nitrogen is split off in the form of ammonia.

The study of this reduction will be continued. Electrolytic reduction experiments yielded no satisfactory results on preliminary trials.

I am now studying the substitution of positive and negative groups in the benzene ring of this acid oil, to determine the effects on the stability and acid properties of the substance. It is hoped that an analogously constituted body may be obtained, of slightly greater stability, upon which a careful study may be made of the manner in which the molecule breaks up under the influence of heat, alkalies, etc.

ON THE ACIDS OF THE FAT OF THE CALIFOR-
NIA BAY TREE.

BY J. M. STILLMAN AND E. C. O'NEILL.

In 1882 we published[1] a summary of a brief examination of
the fatty acids of the seeds of the California Bay Tree (*Um-
bellularia Californica* in which we presented evidence of the
existence of an acid, $C_{11}H_{22}O_2$. The work was interrupted by
the departure of one of us (J. M. S.) for residence in the
Atlantic States, and by the absorption of our interests in other
directions. On account of the anomalous position which the
acid named seemed to hold as the only naturally-occurring
fatty acid of this series with an odd number of carbon atoms,
it seemed to us of importance to investigate more completely
this fat, and finding ourselves, after many years, again in a
position to pursue the examination, we prepared some time
ago a much larger quantity of the fat than was at our disposal
in the first examination, and subjected the free acid to re-
peated distillations. The result of our examination thus has
been to satisfy us that in spite of the experimental evidence
contained in our previous publication and which seemed to
us to warrant the conclusions drawn, we were dealing with a
mixture and not a homogeneous acid. That lauric acid is
present is certain. It has been isolated by each of us, but it
is mixed with other acids from which we had difficulty in
separating it by distillation and by other methods, and we
were deceived by the constancy of the analytical data ob-
tained in our first examination of the acids and the salts and
ethers obtained from them, into the belief that we were deal-
ing with a homogeneous acid.

The reference by Caspari[2] to our former work, in connec-
tion with his examination of the fatty acids of *Lindera Ben-
zoin*, seems to render this explanatory note advisable in ad-
vance of more complete data.

APRIL 22, 1902.

[1] This JOURNAL, **4**, 206.
[2] *Ibid.*, **27**, 291.

REVIEWS.

FIRST BOOK OF QUALITATIVE CHEMISTRY, FOR STUDIES OF WATER SOLUTION AND MASS ACTION. By A. B. PRESCOTT, PH.D., and E. C. SULLIVAN, PH.D., of the University of Michigan. Eleventh edition, entirely rewritten. New York : D. Van Nostrand Co. 1902. Price, $1.50.

The first edition of this book appeared in 1879 and the present edition has been rewritten in the light of the recent views regarding reactions in water solutions. It is to be used as a guide to qualitative analysis and whenever possible the reactions are regarded as reactions of the free ions and explained on this basis. With this exception the book is similar in its general method of presentation to others upon the same subject, each group being treated in order, the general reactions of the separate metals and methods for their separation following in regular order.   J. E. G.

ELEMENTARY ORGANIC ANALYSIS. THE DETERMINATION OF CARBON AND HYDROGEN. By F. G. BENEDICT, PH.D., Instructor in Chemistry in Wesleyan University. Easton, Pa. : The Chemical Publishing Co. 1900. Price, $1.00.

As the author justly remarks in his preface, '' Perhaps no analytical operation is at once so fundamentally important and exasperatingly vexatious as organic combustion. As a rule, a knowledge of the operation is chiefly obtained by word of mouth'' and perhaps even more by bitter experience. There is probably no operation carried out by a student of quantitative analysis which is so dependent upon experience as organic combustion, but the reviewer is heartily in sympathy with the idea of the author who says that '' This little manual is presented in the hope that the descriptions of processes here recorded will aid in making this method of analysis more familiar and more satisfactory.'' The author describes the method of preparation of the various parts of the apparatus and the method of procedure with great care as regards details, and where a number of modifications have been suggested for the same purpose he describes the ones which have given the greatest satisfaction in his experience with over 2,000 combustions.

A careful reading of this little book will no doubt save a beginner in organic analysis many failures and enable him to work more intelligently and independently of the instructor or fellow-students at every step.   J. E. G.

AMERICAN

CHEMICAL JOURNAL

A STUDY OF THE CONDUCTIVITY OF CERTAIN
SALTS IN WATER, METHYL, ETHYL, AND
PROPYL ALCOHOLS, AND IN MIXTURES
OF THESE SOLVENTS.[1]

By Harry C. Jones and Charles F. Lindsay.

INTRODUCTION.

Ever since the birth of the Arrhenius theory of electrolytic
dissociation and the perfection of the Kohlrausch method for
the measurement of the conductivity of solutions, the deter-
mination of the dissociation of electrolytes in aqueous solution
has been the subject of extensive investigation. The work,
however, has been almost exclusively confined to aqueous
solutions, due to the fact that water is a solvent for so many
substances, that it is a very good dissociant, and that it can
readily be purified.

During the last few years, however, the measurement of
dissociation has been extended, to a greater or less extent, to
solutions in many solvents both inorganic and organic, and in
some cases very interesting results have been obtained.

The study of non-aqueous solutions has led to a comparison of the dissociating power of the various solvents, and this in turn has given rise to several generalizations attempting to connect dissociating power with other physical and chemical properties of solvents.

J. J. Thomson[1] and Nernst[2] have sought to connect the dissociating power of a solvent with its dielectric constant. Nernst says: '' The greater the dielectric constant of a medium the greater becomes its electrolytic dissociation of dissolved substances under exactly similar conditions.''

J. J. Thomson, after showing that molecules condensed on the surface of a conducting sphere will be completely dissociated, goes on to say: ''The same effect would be produced by a substance possessing a very large specific inductive capacity. Since water is such a substance it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in solution the forces between them are very much less than they are when the molecule is free and in the gaseous state.''

Brühl[3] showed that while certain organic bodies as the oximes and the alcohols exist in a polymerized state in hydrocarbons, chloroform, or carbon bisulphide solution, the molecular complexes are more or less broken down in water solution, and to a less extent in alcohols, ethers, esters, ketones, and phenols. All of these also exert more or less dissociating power. According to his theory of the tetravalence of oxygen they are unsaturated compounds, and it is to this unsaturation that he ascribes dissociating power. He also attributes the dissociating power of solvents containing nitrogen to the fact that in these compounds nitrogen exists as a triad while it has the power of becoming pentavalent. He predicted dissociating power for compounds containing trivalent nitrogen, including the hydrazines, the amines, the diazo compounds, and liquid hydrocyanic acid, and even for other classes of unsaturated compounds as the trichlorides of

[1] Phil. Mag., **36**, 320.
[2] Ztschr. phys. Chem., **13**, 531.
[3] *Ibid.*, **18**, 514; **27**, 319; **30**, 1; Ber. d. chem. Ges., **28**, 2847, 2866; **30**, 163.

arsenic and phosphorus, the mercaptans, and alkyl sulphides. This prophecy is borne out, to some extent at least, by the later work of Walden. In his last paper Brühl has sought rather to connect dissociating power with a high dielectric constant, and with the tautomerizing power of the solvent.

Ciamician[1] concluded that dissociating power is a function of the chemical properties of the substance, and that those substances which resemble water chemically, as methyl and ethyl alcohol, should have the greatest dissociating power.

Konowalow,[2] from a study of the conductivity of the compounds which amines form with acids, holds that only those solutions conduct in which there is chemical action between the solvent and the dissolved substance.

Dutoit and Aston[3] advanced the idea that dissociating power is related to the amount of the polymerization of the solvent. Water and the alcohols which are good dissociants are also polymerized molecules, as shown by the surface-tension method of Ramsay and Shields.[4]

For further views on this subject consult the paper by Crompton.[5]

Donnan[6] says : '' In a solution in which the solute is more or less ionized, one might suppose the ions to be surrounded by clusters of solvent molecules which had, so to speak, condensed around them, and opposed an obstacle to their recombination. Now one might suppose this state of things as being caused by some sort of specific attraction between the solvent molecules and electricity, *i. e.*, the electrons or electrical charges which are associated with the ions. Were this the case, one might expect this specific attraction to manifest itself in other ways. For example, if electrical nuclei were present in, or were produced by any means in air which was saturated with the vapor of an ionizing liquid, then it would be just possible that the specific attraction referred to above

[1] Ztschr. phys. Chem., **6**, 403.

[2] Wied. Ann., **49**, 733.

[3] Compt. rend., **125**, 240. See also Dutoit and Friderich : Bull. Soc. Chim., [3], **19**, 321.

[4] Ztschr. phys. Chem., **12**, 433.

J. Chem. Soc., **71**, 925.

Phil. Mag , [6], **15**, 305.

might help to produce condensation of the vapor around these nuclei under suitable conditions, *i. e.*, if the vapor were super-saturated by a sudden adiabatic expansion. If the liquid in question did not act as an ionizing solvent, it would be natural to expect that the condensation just alluded to would only occur when the vapor entered the really unstable (labile) region, or at any rate would only be produced by a much higher degree of supersaturation.'' From his experiments, however, he does not feel warranted in drawing any final conclusion.

PART I.

HISTORICAL SKETCH.

A review of the work done on the dissociating power of different solvents has recently been published by one of us in this JOURNAL.[1] Brief reference is given below to work carried out subsequent to the review in question.

Water has always been regarded as the best dissociant, but within the last few months another solvent, liquid hydrocyanic acid, has been found to produce greater dissociation.

Hydrocyanic Acid.—Schlundt[2] has measured the dielectric constant of liquid hydrocyanic acid and found the very large value of 95 at 21°, a value which exceeds that of water, which is 80 at the same temperature. It was, therefore, important, as bearing on the Nernst-Thomson theory of dissociation, that measurements of the conductivity of solutions in this solvent be made. This has been done by Centnerszwer[3] with the result that not only do solutions in hydrocyanic acid show greater conductivity, but the dissociation is also greater than in water. The substances worked with were potassium iodide and trimethylsulphonium iodide. Their conductivity at 0° was nearly the same as the conductivity of aqueous hydrochloric acid at 25°.

Sulphur Dioxide.—Walden and Centnerszwer[4] have very recently published the results of an extensive investigation on

[1] Jones : This JOURNAL, **25**, 232.
[2] J. Phys. Chem., **5**, 157.
[3] J. Russ. phys. chem. Soc., **33**, 545-549 ; Ztschr. phys. Chem., **39**, 217.
[4] Jones : Ztschr. phys. Chem., **39**, 513.

sulphur dioxide as a solvent. This is an extension of the older work of Walden.[1] They investigated the conductivity of nineteen salts, consisting of iodides, bromides, chlorides, and sulphocyanates of inorganic and organic bases. They show, first, that while in aqueous solution the molecular conductivities at 25° of monobasic halogen salts generally lie between 100 and 140, the corresponding values in sulphur dioxide vary between 3 and 157; second, that Kohlrausch's law of the independent migration velocities of the ions does not hold for solutions in sulphur dioxide. They have also shown by a series of conductivity measurements at different temperatures between —78° and 157° (the freezing-point and critical temperature of sulphur dioxide) that the molecular conductivity at first increases with the temperature, passes through a maximum, and then diminishes as the critical temperature is approached. This is seen at once to be just what would be expected from the polymerized solvent theory of Dutoit and Aston. As the temperature rises the association of the solvent decreases, and this would be expected to diminish the ionizing power. They have also determined the molecular weights of a number of electrolytes (salts) in liquid sulphur dioxide by the boiling-point method, reaching the remarkable result that many of these salts show a molecular weight greater than normal, or what is the same thing, the value of the van 't Hoff coefficient "i" is less than unity. This they endeavor to show is due to the fact that, in addition to the electrolytic dissociation, an association takes place in the sulphur dioxide solutions. Facts similar to the maximum value in the temperature-conductivity curve, and to the abnormal values of the van 't Hoff coefficient "i" were noticed by Franklin and Kraus[2] in their work on liquid ammonia.

The remaining work on inorganic solvents we owe chiefly to Walden.[3] He has investigated the solvent and ionizing power of the following compounds : Phosphorus trichloride, phosphorus tribromide, phosphorus oxychloride, arsenic trichloride, antimony trichloride, antimony pentachloride, boron

[1] Ber. d. chem. Ges., **32**, 2862.
[2] This JOURNAL, **20**, 836; **24**, 83.
[3] Ztschr. anorg. Chem., **25**, 209; **29**, 371.

trichloride, silicon tetrachloride, tin tetrachloride, sulphur monochloride, sulphuryl chloride, thionyl chloride, sulphur trioxide, and liquid bromine. Of these, sulphur monochloride, sulphuryl chloride, thionyl chloride, phosphorus oxychloride, arsenic trichloride, and antimony trichloride show considerable ionizing power, while solutions in the remaining solvents exhibit only the very slightest conductivity. In his next paper Walden adds a study of arsenic tribromide, chlorsulphuric acid, sulphuric acid, and the dimethyl ester of sulphuric acid. All of these show a strong tendency to ionize dissolved electrolytes. It is important to notice from this work of Walden that there appears to be no connection between dissociating power and chemical constitution. Antimony pentachloride does not dissociate electrolytes, while the trichloride dissociates to a very considerable extent. On the other hand, phosphorus trichloride does not dissociate, while phosphorus oxychloride does. It is thus evident that among the inorganic solvents, at least, a knowledge of the dissociating power of one solvent tells us nothing as to the dissociating power of substances closely related chemically.

Of the remaining work little need be said. Oddo[1] has also shown that phosphorus oxychloride strongly ionizes electrolytes. Tolloczko,[2] as well as Gareili and Bassani,[3] have worked with the halides of arsenic and antimony, showing them to have ionizing power. Kahlenberg and Lincoln[4] studied solutions of ferric chloride, antimony trichloride, bismuth trichloride, and mercuric chloride in phosphorus trichloride and arsenic trichloride, with results which confirm those mentioned above. Centnerszwer[5] is authority for placing cyanogen among the solvents which do not dissociate. Frankland and Farmer[6] have also shown that nitrogen peroxide does not dissociate, while Skilling[7] has shown that solutions in hydrogen sulphide show no conductivity.

The following table of inorganic solvents is given to show

[1] Atti R. Accad. dei Lincei Roma, [5], 10, 452.
[2] Ztschr. phys. Chem., 30, 705.
[3] Atti R. Accad. dei Lincei Roma, [5], 10, 255.
[4] J. Phys. Chem., 3, 12.
[5] Ztschr. phys. Chem., 39, 217.
[6] J. Chem. Soc., 79, 1356.
[7] This JOURNAL, 26, 383.

what relations exist between dissociating power, dielectric constants, and the association factor :

Inorganic Solvents Which Effect Dissociation.

Solvent.	Dielectric constant.	Association factor.	Considered as
Hydrocyanic acid	95	?	saturated
Water	81.12	3.7	"
Ammonia	16.2	1.0	unsaturated
Sulphur dioxide	13.75	1.0	"
Nitric acid	?	1.7–1.9	saturated
Arsenic trichloride	12.35	?	unsaturated
Arsenic tribromide	?	?	"
Phosphorus oxychloride	13.9	1.00	saturated
Antimony trichloride	33.2	?	unsaturated
Thionyl chloride	9.05	1.08	"
Sulphuryl chloride	9.15	0.97	saturated
Dimethyl sulphate	?	?	"
Chlorsulphuric acid	?	?	"
Sulphuric acid	?	32.0	"
Sulphur monochloride	4.8	0.95–1.05	unsaturated

Inorganic Solvents Which Do Not Dissociate Electrolytes.

Bromine	3.18	1.2–1.3	saturated
Cyanogen	2.52	?	"
Sulphur trioxide	3.56		"
Boron trichloride	?	?	"
Phosphorus trichloride	3.36	1.02	unsaturated
Phosphorus tribromide	?	?	"
Antimony pentachloride	3.78	?	saturated
Silicon tetrachloride	?	1.06	"
Tin tetrachloride	3.2	?	"
Hydrogen sulphide	?	?	"
Nitrogen peroxide	?	?	"

The values for the association factors are taken from the researches of Ramsay and Shields[1] and Ramsay and Aston,[2] while those for the dielectric constants are almost wholly taken from the work of Turner.[3]

Mixed Solvents.

Hydrogen Dioxide and Water.—The dielectric constant of a

[1] Ztschr. phys. Chem., **12**, 433.

[2] J. Chem. Soc., **65**, 167.

[3] J. Phys. Chem., **5**, 503.

mixture of hydrogen dioxide and water is greater than that of pure water. This has been shown by Calvert,[1] and would lead one to suspect that electrolytes dissolved in such mixtures would have a greater conductivity than in pure water, in accordance with the Thomson-Nernst rule. The dissociating power of such mixtures has, however, not yet been determined. Reference should also be made to the later work of Calvert,[2] showing that hydrogen dioxide has acid properties, and to the work of Jones, Barnes, and Hyde[3] along the same lines.

Mixtures of Water and the Alcohols.—Only brief mention need be made of the work of Lenz,[4] Kerler,[5] Stephan,[6] Kablukoff,[7] Carrara,[8] Schall,[9] and Arrhenius.[10] Wakeman,[11] in quite an elaborate investigation, measured the conductivity of organic acids in mixtures of ethyl alcohol and water in varying proportions. The results show that the conductivity becomes gradually smaller as the amount of alcohol becomes larger and larger. This is just what would be expected from the relative conductivities in these two solvents.

Zelinsky and Krapiwin[12] have, however, obtained results of a very different character. They found that the salts with which they worked, when dissolved in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol, gave a conductivity considerably less than the conductivity in either alcohol or water.

Similar results were obtained by Cohen[13] with ethyl alcohol and water, but only when the mixture contained very little water, and at dilutions which were quite large, as is shown by the following table :

[1] Ann. der Phys., **1**, 483.
[2] Ztschr. phys. Chem., **38**, 513.
[3] This Journal, **27**, 22.
[4] Mem. de l'Acad. de St. Petersbourg, [7], **30**, 1881.
[5] Dissertation (Erlangen), 1884.
[6] Wied. Ann., **17**, 673.
[7] Ztschr. phys. Chem., **1**, 432.
[8] Gazz. chim. ital., **16**, 1.
[9] Ztschr. phys. Chem., **14**, 701.
[10] *Ibid.*, **9**, 487.
[1] *Ibid.*, **11**, 49.
[12] *Ibid.*, **21**, 35.
[13] *Ibid.*, **25**, 31.

Potassium Iodide.

v.	Pure alcohol. μ_v 18°.	80 per cent alcohol. μ_v 18°.
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

From an examination of the above results it is seen that the conductivities in the mixtures of water and alcohol are the greater until a dilution of 512 liters is reached. At greater dilutions the conductivity in the pure alcohol becomes greater than that of the alcohol containing 20 per cent of water.

In general, however, Cohen found that addition of water increased the conductivity, as we would expect.

PART II.

EXPERIMENTAL.

This work was undertaken as an extension of the older work of Zelinsky and Krapiwin,[1] and Cohen,[2] on the conductivity of electrolytes in mixtures of methyl and ethyl alcohol with water. Zelinsky and Krapiwin, in their work, have shown that solutions in a 50 per cent mixture of methyl alcohol and water have a much less conductivity than in the pure alcohol itself. They have also shown that the slightest addition of water to a solution of an electrolyte in absolute methyl alcohol produced a lowering of its conducting power.

We have extended this work by making conductivity measurements of solutions in which the solvents have been mixtures of methyl alcohol and water of varying composition. By this means we have been able to plot curves showing for each salt with which we have worked, the mixture of methyl alcohol and water having the least dissociating power.

We have also worked with ethyl alcohol, propyl alcohol, and with mixtures of ethyl alcohol and water, propyl alcohol and water, and of methyl and ethyl alcohols.

[1] *Loc. cit.*
[2] *Loc. cit.*

The work has, for the most part, been done both at 0° and 25°. In this way we have been able to calculate the temperature coefficients of conductivity of the various salts in the different solvents and, what is of more importance, to show the influence of temperature on the minimum values mentioned above.

The salts used are potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, ferric chloride, and lithium nitrate.

Apparatus.

In all this work the Kohlrausch method of measuring conductivity was employed. The bridge wire used was a meter in length and made of "manganin." The resistance coils
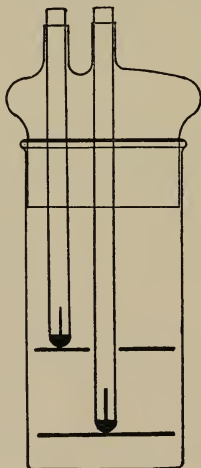
Fig. I.

were manufactured by Leeds & Co., of Philadelphia, and were guaranteed accurate to 1/25 of 1 per cent.

The cells used were of the following form (Fig. I.), the difference between them and the ordinary Arrhenius cell being that they are provided with a ground-glass top to

prevent evaporation of the more volatile solvents, and to protect the anhydrous alcohols from the moisture of the baths and air. In some cases the ground-glass joint was also covered with paraffin as an extra precaution.

The glass tubes carrying the electrodes were shoved through thin rubber tubes, and then inserted into the glass tubes in the cap. Sealing wax was then run over the outside of the joint.

The zero-bath was prepared as follows : A large glass battery-jar was filled with pure, finely crushed ice, and moistened with distilled water. This was placed in a water-bath, the space between the two being filled with finely crushed ice. By this means it was possible to keep a cell within $0°.02$ of zero for hours. The $25°$ bath was of the ordinary form and was stirred by means of a small hot-air engine.

The thermometers used were graduated to $0°.04$ and were carefully calibrated. The burettes and flasks were also carefully calibrated.

Solvents.

Water.—All the water used in this work was purified as follows : Ordinary distilled water was first distilled from acidified potassium bichromate. This water was redistilled from potassium bichromate acidified with sulphuric acid, and then from barium hydroxide. The water purified in this way has a conductivity of never more than 2×10^{-6} and sometimes as low as 0.8×10^{-6}.

Methyl Alcohol.—The methyl alcohol used was the best commercial article which could be obtained. It was first boiled with calcium oxide, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate and then from sodium. None of the alcohol used in making up the absolute alcohol solutions had been distilled from sodium more than twenty-four hours before use. It had a conductivity of about 2.3×10^{-6}.

Ethyl Alcohol.—The ethyl alcohol was the best obtainable article and was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 2×10^{-7}.

Propyl Alcohol.—The propyl alcohol was Kahlbaum's best,

and before use was distilled from anhydrous copper sulphate and sodium. It had a conductivity of 0.8 × 10⁻⁷.

Solutions.

The method of making up the original mother-solutions will be given when the various electrolytes are considered.

From this mother solution the remaining solutions were made by successive dilutions by means of burettes and measuring-flasks. In the cases where this would necessitate the use of small quantities of the solution a second mother-solution was made, and from this successive dilutions were prepared.

In preparing the solutions in the mixed solvents a sufficient quantity of the solvent was made by mixing the constituents in the required proportions. This was then used in the same manner as a simple solvent.

In preparing these mixed solvents the following method was used: "x" cc. of an alcohol were diluted to 100 cc. In the following discussion such a solution would be designated as — alcohol x per cent. In making mixtures of methyl alcohol and ethyl alcohol, the methyl alcohol was measured and diluted with the ethyl alcohol, and the concentration expressed in terms of the methyl alcohol.

Conductivity Measurements.

In all determinations of conductivity from three to five different resistances were used, and the values given in the tables are the mean of these values.

Potassium Iodide.

The salt used in this work was recrystallized a number of times. It was then carefully dried and kept in a desiccator. All the mother-solutions were made by direct weighing.

Table 1.—Molecular Conductivity of Potassium Iodide in Water.

Potassium iodide, KI. Molecular weight, 166.00.

$v.$	μ_v 0°.	μ_v 25°.
64	74.09	132.1
128	76.4 D	135.4
256	77.01	138.0
512	78.0 D	139.6
1024	77.96	140.7

The values of the conductivity at 0° marked "D" were obtained by Jones and Douglas,[1] while those at 25° are taken from the work of Ostwald.

Table II.—Molecular Conductivity of Potassium Iodide in Ethyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	19.12	29.40
128	21.36	33.02
256	22.66	36.02
512	25.00	38.63
1024	27.43	41.35

Table III.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol.

v.	μ_v 0°.	μ_v 25°.
64	59.32	82.87
128	63.88	88.49
256	67.73	93.73
512	69.85	98.36
1024	71.23	102.0

The conductivity of solutions of potassium iodide in methyl alcohol had already been determined by both Zelinsky and Krapiwin,[2] and Carrara,[3] but with such different results that the above measurements seemed necessary. Our measurements agree very well with those of Zelinsky and Krapiwin, as is seen from the following table:

Table IV.—Molecular Conductivity of Potassium Iodide in Methyl Alcohol.

v.	μ_v 25°. Carrara.	μ_v 25°. Zelinsky and Krapiwin.
64	78.7	82.52
128	84.7	88.69
256	88.2	93.85
512	90.8	98.19
1024	93.0	102.2

[1] This JOURNAL, **26**, 428.
[2] Ztschr. phys. Chem., **21**, 35.
[3] Gazz. chim. ital., **26**, (1), 119.

Table V.—*Molecular Conductivity of Potassium Iodide in Methyl Alcohol (20 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	45.69	91.91
128	47.26	93.78
256	47.79	95.64
512	48.45	97.12
1024	49.07	98.10

Table VI.—*Molecular Conductivity of Potassium Iodide in Methyl Alcohol (40 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	35.48	72.14
128	35.92	73.69
256	36.52	75.14
512	37.02	76.25
1024	37.85	77.68

Table VII.—*Molecular Conductivity of Potassium Iodide in Methyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	33.73	67.46
128	34.44	68.79
256	35.13	70.37
512	36.05	71.72
1024	36.76	72.57

Table VIII.—*Molecular Conductivity of Potassium Iodide in Methyl Alcohol (65 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	35.12	65.04
128	35.71	67.25
256	36.49	68.78
512	37.23	70.00
1024	37.75	70.94

Table IX.—*Molecular Conductivity of Potassium Iodide in Methyl Alcohol (80 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	39.03	67.78
128	40.51	70.33
256	41.83	71.83
512	43.23	73.16
1024	44.45	74.81

Table X.—*Molecular Conductivity of Potassium Iodide in Ethyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
64	19.26	48.30
128	19.82	50.07
256	20.35	50.80
512	20.92	51.97
1024	21.43	52.52

Table XI.—*The Molecular Conductivity of Potassium Iodide, Methyl Alcohol (50 Per Cent) and Ethyl Alcohol.*

v.	μ_v 0°.	μ_v 25°.
64	36.74	54.18
128	39.46	58.52
256	41.93	62.13
512	44.46	65.93
1024	46.89	69.61

Table XII.—*Temperature Coefficients of Conductivity of Potassium Iodide in Water (0°–25°).*

v.	Temperature coefficient.
64	2.26
128	2.30
256	2.35
512	2.40
1024	2.52

Table XIII.—*Temperature Coefficients of Conductivity of Potassium Iodide in Methyl Alcohol (0°–25°).*

v.	Temperature coefficient.
64	0.942
128	0.984
256	1.04
512	1.14
1024	1.23

Table XIV.—*Temperature Coefficients of Conductivity of Potassium Iodide in Ethyl Alcohol (0°–25°).*

v.	Temperature coefficient.
64	0.411
128	0.466
256	0.534
512	0.545
1024	0.557

Table XV.—Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water of Various Compositions.

v.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.
64	1.83	1.47	1.35	1.17	1.15
128	1.86	1.51	1.37	1.26	1.17
256	1.91	1.54	1.41	1.29	1.20
512	1.95	1.57	1.43	1.31	1.20
1024	1.96	1.59	1.43	1.32	1.21

Table XVI.—Temperature Coefficients of Conductivity of Potassium Iodide in a 50 Per Cent Mixture of Ethyl Alcohol and Water (0°–25°).

v.	Temperature coefficient.
64	1.16
128	1.25
256	1.22
512	1.24
1024	1.24

Table XVII.—Temperature Coefficients of Conductivity of Potassium Iodide in a 50 Per Cent Mixture of Methyl and Ethyl Alcohols (0°–25°).

v.	Temperature coefficient.
64	0.698
128	0.762
256	0.808
512	0.859
1024	0.909

In order to see the connection existing between the conducting power of the solutions in the various solvents, the following tables are given for the sake of comparison :

Table XVIII.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 0°.

v.	0 per cent.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.	100 per cent.
64	74.09	....	35.48	33.73	35.12	39.03	59.32
128	76.4 D	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.0 D	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

The values in this table are plotted in Fig. II. It is seen that the values of the molecular conductivity reach a mini-

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Potassium Iodide
in
Water, Methyl
Alcohol,
and
Mixtures
at 0°.
Curve I V=64
II V=128
III V=256
IV V=512
V V=1024

Strength of Alcohol
0%   20%   40%   60%   80%   100%

Fig. II.

mum in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol.

It is also seen that an addition of approximately 10 per cent of alcohol lowers the conductivity of the water solutions to that of an alcoholic solution.

Table XIX.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents, at 25°.

v.	0 per cent.	20 per cent.	40 per cent.	50 per cent.	65 per cent.	80 per cent.	100 per cent.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0
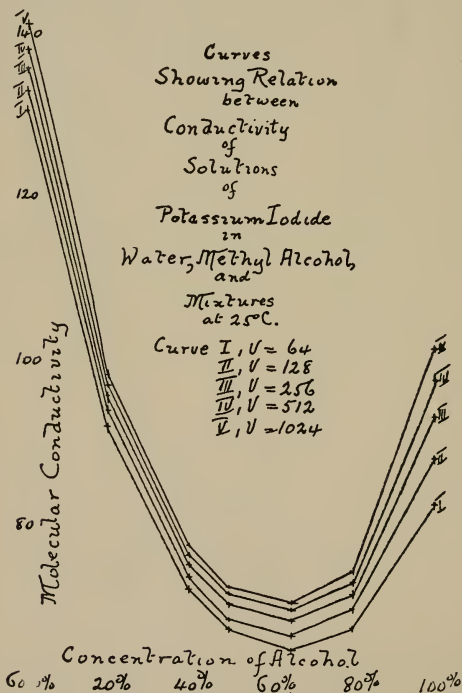
Fig. III.

The results given in this table are plotted in Fig. III. The curves are of the same general form as the preceding. The chief points of difference are : (1) The minimum point has shifted to the right, corresponding now to an alcohol-water mixture of about 65 per cent. The increase to the right of the minimum is much less rapid than that to the left, the difference being due to the fact that the temperature coefficient of conductivity is much greater in water than in methyl alcohol. The alcohol-water mixture having the same conducting power as the solution in pure methyl alcohol has also changed. In this case it changes from an alcohol of about 19 per cent to an alcohol of about 30 per cent, depending upon the concentration of the solution.

Table XX.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 0°.

	Water.	Mixture.	Ethyl alcohol.
v.	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	74.09	19.26	19.12
128	76.4	19.82	21.36
256	77.01	20.35	22.66
512	78.0	20.92	25.00
1024	77.96	21.43	27.43

Table XXI.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 25°.

	Water.	Mixture.	Ethyl alcohol.
v.	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	132.1	48.30	29.40
128	135.4	50.07	33.02
256	138.0	50.80	36.02
512	139.6	51.97	38.63
1024	140.7	52.52	41.35

Cohen[1] has shown that solutions of potassium iodide in a mixture of alcohol and water show a minimum in the conductivity, but only at great dilutions (512), and when the amount of water present is small. His work, however, was all done at 18° C. From the results in Table XX. we see that at 0°

[1] Ztschr. phys. Chem., **25**, 31.

we have a minimum in the conductivity values for an alcohol as dilute as 50 per cent, and in solutions which are comparatively strong, namely from $v = 128$. In all probability in alcohol of 75 to 80 per cent a much greater depression would be found. This is, however, a subject for future investigation. At 25° all trace of a minimum has disappeared.

Table XXII.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 0°.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
$v.$	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	59.32	36.74	19.12
128	63.88	39.46	21.36
256	67.73	41.93	22.66
512	69.85	44.46	25.00
1024	71.23	46.89	27.43

Table XXIII.—Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 25°.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
$v.$	$\mu_v.$	$\mu_v.$	$\mu_v.$
64	82.87	54.18	29.40
128	88.49	58.52	33.02
256	93.73	62.13	36.02
512	98.36	65.93	38.63
1024	102.0	69.61	41.35

The last two tables make it clear that in a mixture of methyl and ethyl alcohols, the conductivity of potassium iodide shows no minimum value when compared with the conductivity in the pure solvents. In fact, the conductivity values for the solutions in the mixed solvent approach the mean value of the conductivities in the pure solvents. Thus, at 0° the observed value of the conductivity in the mixture, for $v = 64$, is 36.74, while the mean of the conductivities at the same dilution in the pure solvents is 39.22. In all cases, however, the conductivity in the mixture lies below this mean value.

Ammonium Bromide.

The salt used in this work was carefully recrystallized, and on sublimation left no residue. It was thoroughly dried and kept in a desiccator. All the mother solutions were made by direct weighing.

Table XXIV.—Molecular Conductivity of Ammonium Bromide in Water.

Ammonium bromide, NH_4Br. Molecular weight, 98.04.

$v.$	$\mu_v\ 0°.$	$\mu_v\ 25°.$
64	74.22	135.3
128	75.23	138.6
256	76.62	141.2
512	77.49	143.5
1028	77.78	145.6

Table XXV.—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol.

$v.$	$\mu_v\ 0°.$	$\mu_v\ 25°.$
64	58.71	79.56
128	63.16	85.80
256	66.45	90.88
512	68.51	94.99
1024	70.40	98.24

The values at 25° in these two tables are all taken from the work of Zelinsky and Krapiwin.

Table XXVI.—Molecular Conductivity of Ammonium Bromide in Ethyl Alcohol.

$v.$	$\mu_v\ 0°.$
64	16.71
128	18.83
256	19.66
512	22.66
1024	22.88

Table XXVII.—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol (50 Per Cent) and Water.

$v.$	$\mu_v\ 0°.$
64	34.85
128	35.78
256	36.36
512	37.11
1024	37.49

Table XXVIII.—*Molecular Conductivity of Ammonium Bromide in Ethyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.
64	19.42
128	19.89
256	20.09
512	20.70
1024	21.50

Table XXIX.—*Molecular Conductivity of Ammonium Bromide in Methyl Alcohol (50 Per Cent) and Ethyl Alcohol.*

v.	μ_v 0°.
64	34.15
128	38.40
256	39.75
512	41.06
1024	42.00

Table XXX.—*Temperature Coefficients of Conductivity of Ammonium Bromide in Water (0°–25°).*

v.	Temperature coefficient.
64	2.44
128	2.54
256	2.58
512	2.64
1024	2.71

Table XXXI.—*Temperature Coefficients of Conductivity of Ammonium Bromide in Methyl Alcohol (0°–25°).*

v.	Temperature coefficient.
64	0.834
128	0.906
256	0.977
512	1.059
1024	1.114

Table XXXII.—*Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Methyl Alcohol, and a 50 Per Cent Mixture of these Solvents at 0°.*

v.	Water. μ_v 0°	Mixture. μ_v 0°.	Methyl alcohol. μ_v 0°.
64	74.32	34.85	58.71
128	75.23	35.78	63.16
256	76.62	36.36	66.45
512	77.49	37.11	68.51
1024	77.78	37.49	70.40

Table XXXIII.—Molecular Conductivity of Ammonium Bromide ($v = 64$) in Methyl Alcohol, Water, and Mixtures of These Solvents at $0°$.

Alcohol. Per cent.	μ_v $0°$.
0	74.22
20	47.96
50	34.85
65	34.68
80	40.55
100	58.71

We see that in these results we have practically the same phenomenon as in the case of potassium iodide. In the case of ammonium bromide the minimum point in the conductivity values appears to be reached with an alcohol of 50 per cent.

Table XXXIV.—Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of These Solvents at $0°$.

	Water.	Mixture.	Ethyl alcohol.
v.	μ_v $0°$.	μ_v $0°$.	μ_v $0°$.
64	74.22	19.42	16.71
128	75.23	19.89	18.83
256	76.62	20.09	19.66
512	77.49	20.70	22.66
1024	....	21.50	22.88

From this table we see that here also a 50 per cent ethyl alcohol gives a minimum, but only in the case of the more dilute solutions, namely for dilutions $v = 512$ and 1024.

Table XXXV.—Comparison of the Molecular Conductivity of Ammonium Bromide in Methyl Alcohol, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents at $0°$.

	Methyl alcohol.	Mixture.	Ethyl alcohol.
v.	μ_v $0°$.	μ_v $0°$.	μ_v $0°$.
64	58.71	34.15	16.71
128	63.16	38.40	18.83
256	66.45	39.75	19.66
512	68.51	41.06	22.66
1024	70.40	42.00	22.88

In this comparison there is no trace of a minimum, nor does there appear to be the slightest chance of there being one for any mixture of methyl and ethyl alcohols.

Strontium Iodide.

The strontium iodide used in this work was a sample of Bender and Hobein's best material. It was practically free from impurities. The material was dried as follows: It was carefully heated with a little ammonium iodide in a current of pure, dry hydrogen until all the water and ammonium iodide had been driven off. After cooling in the stream of hydrogen it was at once dissolved. The solutions were perfectly neutral and showed not the slightest coloration with starch solution. No trace of ammonium salts could be detected. The solutions were preserved in the dark in tightly stoppered bottles.

Table XXXVI.—Molecular Conductivity of Strontium Iodide in Water.

Strontium iodide, SrI_2.   Molecular weight, 341.3.

v.	$\mu_v 0°$.	$\mu_v 25°$.
32	113.1	205.3
64	117.7	214.5
128	122.1	223.1
256	126.0	231.8
512	129.8	240.2
1024	132.6	245.9

Table XXXVII.—Molecular Conductivity of Strontium Iodide in Methyl Alcohol.

v.	$\mu_v 0°$.	$\mu_v 25°$.
32	75.82	101.4
64	85.01	115.3
128	94.76	128.6
256	104.4	141.4
512	114.0	153.9
1024	123.4	166.3

Table XXXVIII.—*Molecular Conductivity of Strontium Iodide in Ethyl Alcohol.*

v.	μ_v 0°.	μ_v 25°.
32	17.44	24.00
64	20.28	28.88
128	23.66	33.53
256	27.00	38.88
512	32.07	46.13
1024	36.01	51.25

Table XXXIX.—*Molecular Conductivity of Strontium Iodide in Propyl Alcohol.*

v.	μ_v 0°.	μ_v 25°.
32	4.70	7.58
64	5.62	8.84
128	6.52	10.20
256	7.41	11.32

Table XL.—*Molecular Conductivity of Strontium Iodide in Methyl Alcohol (25 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	63.06	131.3
64	66.05	138.5
128	68.62	145.3
256	70.98	152.3
512	73.10	157.4
1024	75.51	161.9

Table XLI.—*Molecular Conductivity of Strontium Iodide in Methyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	50.19	103.8
64	52.61	109.9
128	55.05	115.3
256	57.18	120.1
512	....	124.3
1024	61.03	128.5

Table XLII.—*Molecular Conductivity of Strontium Iodide in Methyl Alcohol (75 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	55.53	98.09
64	59.24	104.8
128	62.85	111.4
256	66.68	118.0
512	69.98	124.8
1024	73.22	131.4

Table XLIII.—*Molecular Conductivity of Strontium Iodide in Ethyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	28.32	72.51
64	29.72	76.89
128	31.25	80.21
256	32.23	83.21
512	33.22	86.44
1024	34.16	89.32

Table XLIV.—*Molecular Conductivity of Strontium Iodide in Propyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	27.40	67.67
64	28.63	71.63
128	29.83	75.44
256	30.98	79.32

Table XLV.—*Temperature Coefficients of Conductivity of Strontium Iodide in Water (0°–25°).*

v.	Temperature coefficient.
32	3.29
64	3.87
128	4.04
256	4.23
512	4.42
1024	4.53

Table XLVI.—*Temperature Coefficients of Conductivity of Strontium Iodide in Methyl Alcohol (0°–25°).*

v.	Temperature coefficient.
32	1.02
64	1.21
128	1.35
256	1.48
512	1.60
1024	1.72

Table XLVII.—*Temperature Coefficients of Conductivity of Strontium Iodide in Ethyl Alcohol (0°–25°).*

v.	Temperature coefficient.
32	0.262
64	0.344
128	0.396
256	0.475
512	0.562
1024	0.610

Table XLVIII.—*Temperature Coefficients of Conductivity of Strontium Iodide in Propyl Alcohol (0°–25°).*

v.	Temperature coefficient.
32	0.115
64	0.129
128	0.147
256	0.156

Table XLIX.—*Temperature Coefficients of Conductivity of Strontium Iodide in Various Mixtures of Methyl Alcohol and Water.*

v.	25 per cent.	50 per cent.	75 per cent.
32	2.73	2.14	1.70
64	2.90	2.29	1.82
128	3.07	2.41	1.94
256	3.25	2.52	2.05
512	3.37	2.59	2.19
1024	3.45	2.70	2.33

Table L.—*Temperature Coefficients of Conductivity of Strontium Iodide in Ethyl Alcohol (50 Per Cent) and Water (0°–25°).*

v.	Temperature coefficient.
32	1.77
64	1.89
128	1.96
256	2.04
512	2.13
1024	2.21

Table LI.—*Temperature Coefficients of Conductivity of Strontium Iodide in Propyl Alcohol (50 Per Cent) and Water (0°–25°).*

v.	Temperature coefficient.
32	1.61
64	1.72
128	1.82
256	1.93

Table LII.—*Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 0°.*

v.	0 per cent.	20 per cent.	50 per cent.	75 per cent.	100 per cent.
32	113.1	63.06	50.19	55.53	75.82
64	117.7	66.05	52.61	59.24	85.01
128	122.1	68.62	55.05	62.85	94.76
256	126.0	70.98	57.18	66.68	104.4
512	129.8	73.10	59.51	69.98	114.0
1024	132.6	75.51	61.03	73.22	123.4

The results of Table LII. are plotted in Fig. IV. It is

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Strontium Iodide
in
Water, Methyl Alcohol,
and
Mixtures
at 0°.
Curve I, $V = 32$
II, $V = 64$
III, $V = 128$
IV, $V = 256$
V, $V = 572$
VI, $V = 1024$

Molecular Conductivity

Concentration of Alcohol

0%　　25%　　50%　　75%　　100%

Fig IV.

seen that the curve is of identically the same form as that for potassium iodide at the same temperature. The minimum point is reached with an alcohol of about 50 per cent.

Table LIII.—*Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 25°.*

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.8	152.3	120.1	118.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	245.9	161.9	128.5	131.4	166.3
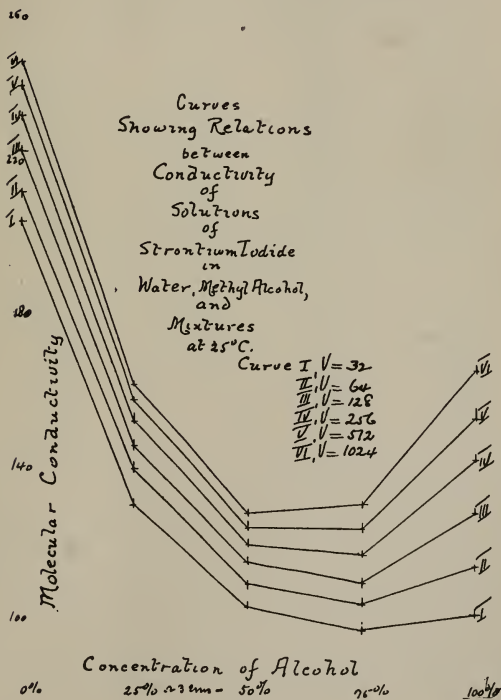
Fig. V.

The results of this table are plotted as Fig. V. It is seen that in this curve the effect of temperature has been such as to almost completely blot out the minimum value in the curve for $v = 32$; and in the other dilutions the minimum is much less pronounced than in the curves thus far studied. The effect of temperature is also to shift the minimum point to the right, the minimum point existing for an alcohol of about 65 to 70 per cent.

Table LIV.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of these Solvents.

0°.

v.	Water. μ_v.	Mixture. μ_v.	Ethyl alcohol. μ_v.
32	113.1	28.32	17.44
64	117.7	29.72	20.28
128	122.1	31.25	23.66
256	126.0	32.23	27.00
512	129.8	33.22	32.07
1024	132.6	34.16	36.01

25°.

32	205.3	72.51	24.00
64	214.5	76.89	28.88
128	223.1	80.21	33.53
256	231.8	83.21	38.88
512	240.2	86.44	46.13
1024	245.9	89.32	51.25

In the table for 0° we see that the values for pure ethyl alcohol are, in the stronger solutions, much smaller than those for the mixture. They, however, increase more rapidly, and in the most dilute solutions pass the values for the mixture, giving us again the minimum point. At 25° there is not the slightest trace of a minimum point, although the values are well below the mean of the values for the pure solvents.

In comparing the values for a mixture of propyl alcohol and water with those for the pure solvents, we find that there is not the slightest trace of a minimum at either 0° or 25°.

Cadmium Iodide.

The cadmium iodide which was used was a sample which had been employed in some previous work in this laboratory, and had then been very carefully purified. The solutions were made by direct weighing.

Table LV.—Comparison of the Molecular Conductivity of Cadmium Iodide in Methyl Alcohol, Water, and a 50 Per Cent Mixture of these Solvents at 25°.

Cadmium iodide, CdI_2. Molecular weight, 366.1.

	Water.	Mixture.	Methyl alcohol.
$v.$	$\mu_v.$	$\mu_v.$	$\mu_v.$
16	62.98	20.31	13.07
32	81.96	24.22	13.59
64	104.7	31.17	14.16
128	129.3	42.03	14.78
256	153.6	50.43	15.44

Table LVI.—Comparison of the Molecular Conductivity of Cadmium Iodide in Varying Mixtures of Methyl Alcohol and Water at 25°.

Concentration of alcohol.	$v = 16.$	$v = 64.$
Per cent.	$\mu_v.$	$\mu_v.$
0	62.98	104.7
50	20.31	31.17
60	....	25.66
80	14.70	18.41
100	13.07	14.16

When the results in the second part of this table are plotted as curves no trace of a minimum appears (Fig. VI.). A considerable difference is, however, noticed between the values obtained and those required from the law of mixtures, the conductivity values obtained being always lower.

Lithium Nitrate.

The lithium nitrate used in this work was a sample from Kahlbaum. It was dried in an air-bath at 150° and kept in a desiccator. The solutions were made by direct weighing.
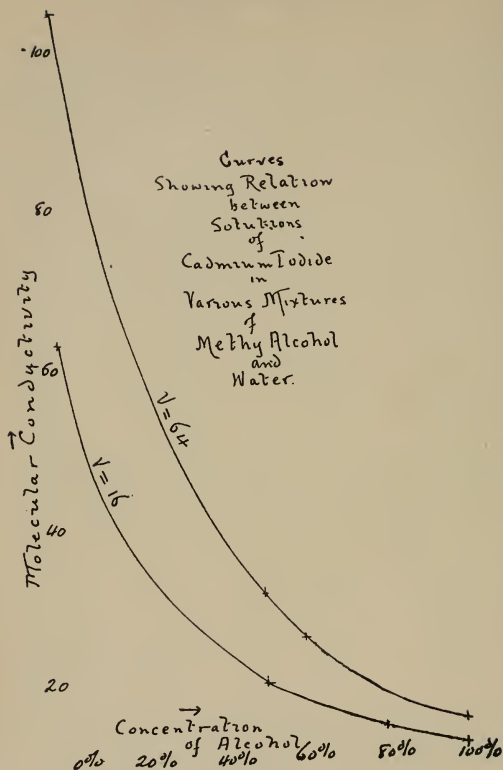
Fig. VI.

*Table LVII.—Molecular Conductivity of Lithium Nitrate in
Water.*

Lithium nitrate, LiNO₃.   Molecular weight, 69.0.

v.	μ_v 0°.	μ_v 25°.	μ_v 25°. (Ostwald.)
32	50.00	91.83	91.8
64	51.49	94.62	94.5
128	52.51	98.00	97.7
256	53.40	99.68	100.0
512	54.70	101.3	101.5
1024	55.30	102.3	102.0

Table LVIII.—*Molecular Conductivity of Lithium Nitrate in Methyl Alcohol.*

v.	$\mu_v\,0°$.	$\mu_v\,25°$.
32	45.97	63.51
64	50.12	69.32
128	53.95	74.51
256	56.67	80.57
512	60.06	83.31
1024	63.40	86.46

From these two tables we see that at 0° the conductivity in pure methyl alcohol, although starting lower than the conductivity in water, increases more rapidly, so that we have solutions in methyl alcohol with greater conductivity than solutions of the same strength in water. That our measurements are accurate is made more probable by the close agreement with Ostwald's values. The solutions measured at 0° were the same as at 25°. The conductivity of a number of the solutions in methyl alcohol was redetermined, using a different sample of an alcohol and salt. In all cases the agreement was all that could be desired.

Table LIX.—*Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol.*

v.	$\mu_v\,0°$.	$\mu_v\,25°$.
32	14.29	21.99
64	15.60	24.85
128	17.52	27.72
256	19.39	30.84
512	21.36	33.25
1024	23.29	35.52

Table LX.—*Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol (50 Per Cent) and Water.*

v.	$\mu_v\,0°$.	$\mu_v\,25°$.
32	13.10	33.73
64	13.56	35.57
128	14.27	37.08
256	14.63	38.85
512	15.45	40.14
1024	16.25	41.35

From Tables LVIII. and LIX. it is seen that with lithium nitrate a minimum point is found in the conductivity values at 0°, and through all the dilutions employed. At 25° no trace of minimum values is apparent.

Table LXI.—*Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (25 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	29.15	60.56
64	29.68	62.16
128	30.15	63.77
256	30.70	64.96
512	31.35	66.78
1024	32.56	69.02

Table LXII.—*Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (50 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	23.59	47.87
64	24.49	49.92
128	25.03	51.50
256	25.71	53.57
512	26.35	54.62
1024	27.35	55.60

Table LXIII.—*Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (75 Per Cent) and Water.*

v.	μ_v 0°.	μ_v 25°.
32	26.67	47.06
64	27.95	49.52
128	28.66	51.64
256	29.51	54.36
512	30.64	56.68
1024	31.91	58.56

Table LXIV.— *Temperature Coefficients of Conductivity of Lithium Nitrate in Water (0°–25°).*

v.	Temperature coefficient.
32	1.67
64	1.72
128	1.82
256	1.85
512	1.86
1024	1.88

Table LXV.—*Temperature Coefficients of Conductivity of Lith-ium Nitrate in Methyl Alcohol* (0°–25°).

v.	Temperature coefficient.
32	0.702
64	0.768
128	0.822
256	0.956
512	0.930
1024	0.922

Table LXVI.—*Temperature Coefficients of Conductivity of Lith-ium Nitrate in Ethyl Alcohol* (0°–25°).

v.	Temperature coefficient.
32	0.308
64	0.370
128	0.408
256	0.458
512	0.476
1024	0.489

Table LXVII.—*Temperature Coefficients of Conductivity of Lith-ium Nitrate in Methyl Alcohol (25, 50, and 75 Per Cent) and Water* (0°–25°).

v.	25 per cent.	50 per cent.	75 per cent.
32	1.25	0.97	0.82
64	1.30	1.01	0.86
128	1.35	1.06	0.92
256	1.37	1.11	0.99
512	1.42	1.13	1.04
1024	1.46	1.13	1.07

Table LXVIII.—*Temperature Coefficients of Conductivity of Lithium Nitrate in Ethyl Alcohol (50 Per Cent) and Water* (0°–25°).

v.	Temperature coefficient.
32	0.83
64	0.88
128	0.91
256	0.97
512	0.99
1024	1.04

Table LXIX.—*Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of these Solvents at o°.*

v.	o per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	50.00	29.15	23.59	26.67	45.97
64	51.49	29.68	24.49	27.95	50.12
128	52.51	30.15	25.03	28.66	53.95
256	53.40	30.70	25.71	29.51	56.67
512	54.70	31.35	26.35	30.64	60.06
1024	55.30	32.56	27.35	31.91	63.40

Table LXX.—*Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of these Solvents at 25°.*

v.	o per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
32	91.83	60.56	47.87	47.06	63.51
64	94.62	62.16	49.92	49.52	69.32
128	98.00	63.77	51.50	51.64	74.51
256	99.68	64.96	53.57	54.36	80.57
512	101.3	66.78	54.62	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

These values, when plotted (Figs. VII. and VIII.), give curves very similar to those already described in connection with potassium iodide and strontium iodide. The only difference worthy of special mention is the fact that at o° the molecular conductivity in methyl alcohol rises above that in water.

Ferric Chloride.

It was desired to make a complete investigation of the changes in the conductivity of solutions of ferric chloride in the various solvents. This was desirable on account of the great solubility of the substance in the different alcohols, and because of the large number of ions into which it can dissociate. This part of the investigation, on account of unexpected difficulties met with, and of the time at our disposal, had to be postponed. Some few observations were, however, made, and these are recorded. The ferric chloride used was prepared as follows: Iron filings, which had been washed with alcohol and ether to remove any adhering grease, were heated in a current of pure, dry chlorine in a large combus-

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Lithium Nitrate
in
Water, Methyl Alcohol,
and
Mixtures
at 0°C.

Curve I. $V = 32$
II. $V = 64$
III. $V = 128$
IV. $V = 256$
V. $V = 512$
VI. $V = 1024$

Molecular Conductivity

Concentration of Alcohol
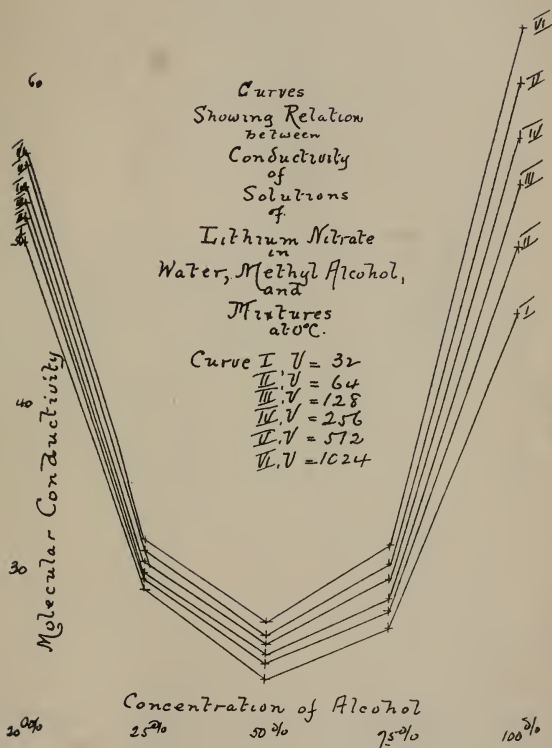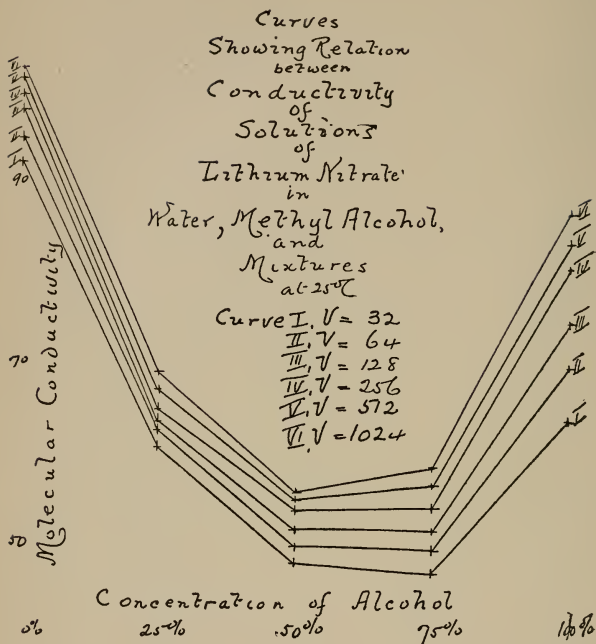
Fig. VII.

Fig. VIII.

tion tube of hard glass. The ferric chloride formed was al-
lowed to distil into a cooled portion of the tube and then it
was redistilled into a wide-mouthed salt bottle. The excess
of chlorine was removed by heating the chloride in a current
of dry nitrogen. The chloride thus formed dissolved com-
pletely in both alcohol and water.

Water solutions were standardized as follows: They were
reduced with zinc and sulphuric acid and the ferrous iron de-

termined with standard potassium permanganate. Alcoholic solutions were first precipitated with aqueous ammonia, filtered, washed, dissolved in a little hydrochloric acid, reduced, and titrated as above.

Table LXXI.—Molecular Conductivity af Ferric Chloride in Water.

Ferric chloride, $FeCl_3$. Molecular weight, 162.35.

v.	$\mu_v \, 0°$.	$\mu_v^- 25°$.
32	163.7	319.2
64	187.0	370.2
128	213.0	422.6
256	240.0	476.7

These values agree fairly well with those of Goodwin,[1] but are in all cases slightly lower, possibly due to the fact that the conductivity of our solutions was measured immediately after standardization, while Goodwin's had been made up for several months. Accurate measurements at a dilution greater than $v = 256$ could not be made, as hydrolysis took place to a very marked extent, as was noticed by Goodwin in the work just referred to.

Table LXXII.— Temperature Coefficients of Conductivity of Ferric Chloride in Water $(0°-25°)$.

v.	Temperature coefficient.
32	6.22
64	7.32
128	8.38
256	9.47

In mixtures of the alcohols and water the same hydrolysis was found to take place, while in the solutions in absolute alcohol a different change occurred. The solution, originally of a pale straw-color, gradually became lighter and lighter when in contact with the platinum black of the electrodes. This was accompanied by a steady rise in the molecular conductivity, which, at the end of twenty-four hours, was still appreciable. The colorless solution showed only the slightest trace of ferric iron, having apparently been reduced to the ferrous condition. These changes are shown in the following tables :

[1] Phys. Rev., **11**, 193 ; Ztschr. phys. Chem., **21**, 1.

Table LXXIII.—*Table Showing the Changes in the Molecular*
Conductivity of Ferric Chloride (v = 512) with Time,
in a Mixture of Methyl Alcohol (50 Per Cent)
and Water.

April 8th. P. M.	μ_v 25°.
12.25	. . . .
12.27	130.1
12.29	135.6
12.31	141.8
12.33	145.4
12.36	150.8
12.38	153.9
12.41	156.3
12.45	159.5
12.56	162.4
1.00	166.7
1.10	169.1
1.30	172.9
2.00	175.0
3.00	180.6
4.00	182.2
5.00	183.0

Table LXXIV.—*Table Showing the Changes in the Molecular*
Conductivity of Ferric Chloride (v = 512) with Time,
in Methyl Alcohol.

April 15th. P. M.	μ_v 25°.
2.15	. . . .
2.18	62.90
2.21	65.47
2.24	67.18
2.28	68.16
2.35	69.64
2.45	71.91
3.00	75.00
3.15	78.06
3.30	81.75
3.46	84.11
4.15	88.59
4.45	92.93
6.15	103.6
April 16th. A. M.	
10.35	132.6
11.15	133.7
P. M.	
2.35	134.3

Summary.

We are led from the preceding study to conclude that the minimum point, discovered by Zelinsky and Krapiwin, is not an isolated phenomenon restricted to the mixtures of methyl alcohol and water, but is much more general. This minimum point in the conductivity has been found for all the salts studied in mixtures of methyl alcohol and water, with the exception of cadmium iodide. Ethyl alcohol and water yield a minimum in the conductivity of all the salts investigated at o°. At 25° this minimum had disappeared. Mixtures of methyl alcohol and ethyl alcohol do not exhibit this phenomenon, but the conductivity of a salt dissolved in a 50 per cent mixture of methyl and ethyl alcohols is less than the mean of the conductivities of the substance in the pure solvents at the same dilution.

To explain these facts one of us[1] advanced tentatively the following suggestion. According to the theory of Dutoit and Aston it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this be true, it is probable, since those substances which dissociate dissolved electrolytes also show in general a normal molecular weight for dissolved non-electrolytes, that this breaking down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either methyl or ethyl alcohol, or a mixture of methyl alcohol and ethyl alcohol. In these cases, since the molecules are less associated than the constituents, we would expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which we have worked this is exactly what has been observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

In support of the above view that one associated solvent

[1] Lindsay.

can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurements. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal, while the surface-tension method of Ramsay and Shields shows, beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the state of aggregation of an associated liquid, it would be expected that at the higher temperature the influence of the solvents on each other would be less than at the lower temperature. That such is the case can be seen by comparing the results at o° with those at 25°.

In conclusion we desire to thank Mr. Kaufman G. Falk for assistance in making the conductivity measurements during the latter part of this investigation.

Chemical Laboratory,
Johns Hopkins Univ.,
May, 1902.

HYDROLYSIS OF TRIACETYLGLUCOSE BY ENZYMES.

By S. F. Acree and J. E. Hinkins.

In a previous article[1] we showed that some bacteria, especially *Bacillus acidi lactici* and *B. sarcina lutea*, when in culture media containing glucose, lactose, etc., generate organic acids, and, furthermore, have the property of causing these organic acids to combine with the sugar to form esters. It was found that, although the bacteria continued to produce acids, the free acid did not increase in quantity, but by titrating the free acid in the cold and then boiling this neutral solution for a short time, more free acid was generated. Hence we quickly guessed that the bacteria, or possibly enzyme-like bodies excreted from them, were causing a part of the free acid to combine with the glucose to form glucose

[1] Read before the International Dental Congress, Paris, Aug. 8, 1900. Dental Cosmos, June, 1901.

esters which, in the cold, were not rapidly saponified by sodium hydroxide, but which, by boiling, were hydrolyzed by the hot water. Hence the amount of the acid combined as ester was determined by titration with N/10 sodium hydroxide after the hydrolysis. Such hydrolysis of ordinary esters or even more complex ones[1] is so well known that it needs no further comment.

Under the conditions of our experiments it was impossible to tell whether the bacteria hydrolyze the glucose esters, as well as cause their formation from glucose and free acids. We afterwards took up this work again with the view of ascertaining if such a reversible process can be realized. Since triacetylglucose can be easily made, and since enzymes, such as pancreatin, emulsin, diastase, etc., can be easily obtained in the market, we began the work by the study of the action of the enzymes on triacetylglucose. We have found that enzymes hydrolyze triacetylglucose into acetic acid and glucose. Furthermore, what few experiments we have carried out in this direction show that the enzymes can also make acetic acid unite with glucose to form esters,—in other words, we have here a reversible process that can be represented as follows when we consider only the formation and hydrolysis of monoacetylglucose, which is, of course, the simplest ester that can be formed by the action of acetic acid on glucose.

$$C_6H_{11}O_5OH + HOOC.CH_3 \rightleftarrows C_6H_{11}O_5CO_2CH_3 + H_2O.$$
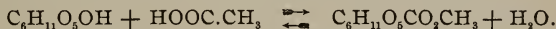
One very important reason for starting first with the action of enzymes (not bacteria) on triacetylglucose is that the enzymes do not act upon the products of hydrolysis, namely, glucose and acetic acid, and hence the determination of the amount of hydrolysis is very simple. *see errata V. 29 p 88*

When a sterilized solution containing 20 grams of glucose and 5 cc. of glacial acetic acid in 1 liter, and which was the N/11.51 acid, was closed and allowed to stand at a constant temperature of 37° C. for thirty days there was no fermentation, nor was there any change in the strength of the acid, as it was shown by titration at the end of this time to have ex-

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[1] Acree : This JOURNAL, **27**, 132; Ber. d. chem. Ges., **35**, 553.

actly the same strength, N/11.51. This same was also true for a part of this solution diluted about three and a half times, so that it was N/37.35 acid. Furthermore, when a 3.2 per cent solution of triacetylglucose, which titrated N/42.44 acid, was left at 0° C. for thirteen days, and kept sterile by means of toluene and thymol, there was no hydrolysis by the water, for titration showed at the end that it was N/42.50. A faintly acid solution of pancreatin was allowed to stand for ten days, but no change in acidity took place. Hence we are very sure that if any changes take place according to the above equation, the enzyme must take part in the reaction or act as a catalytic agent. Hufner,[1] Loew,[2] Nasse,[3] and others, have given us theories to account for the action of ferments, but none are well worked out experimentally. Nasse's hypothesis might be restated as follows: Glucose gives no hydroxyl ions, and hence dilute acetic acid does not act upon it. Suppose that pancreatin has the power to unite with glucose, and that in this double compound the hydroxyl groups of the glucose become hydroxyl ions; then the ionized acetic acid can act upon this double compound, forming water and the double compound, enzyme-acetylglucose, which may break up into the enzyme and acetylglucose. The enzyme which is thus regenerated may then act upon another molecule of glucose (or the acetylglucose), causing other hydroxyl groups to be changed to hydroxyl ions, and hence the process is repeated. If we assume all the above reactions to be reversible, then the hydrolysis of acetylglucose, for instance, would be incomplete. But if some steps in the reaction are non-reversible or practically so, then we might have the reaction going completely in one direction. The entire reaction can be represented as follows:

$$C_6H_{11}O_5OH + HAc^4 + enz. \rightleftharpoons$$
$$enz. \, C_6H_{11}O_5OH + H + Ac \rightleftharpoons$$
$$enz. \, C_6H_{11}O_5 + OH + H + Ac \rightleftharpoons$$
$$enz. \, C_6H_{11}O_5Ac + H_2O \rightleftharpoons$$
$$C_6H_{11}O_5Ac + enz. + H_2O.$$
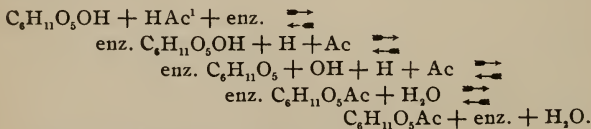
[1] Hufner: J. prakt. Chem., N. F., 10, 385 (1874).
[2] Loew: *Ibid.*, 11, 372 (1875); Pflüg. Archiv., 27.
[3] Nasse: Maly's Jb., 1894, 718.
[4] Ac = CH₃CO₂— ; enz. = enzyme.

Nasse's hypothesis, however, as applied in the above form, does not easily give us an explanation of the oxidation and reduction reactions accomplished by bacteria and enzymes.

If we look through the literature on enzymes, we find isolated cases where enzymes cause the hydrolysis of substances similar to the above. Probably the best piece of work done was published by Kastle and Loevenhart.[1] They showed that lipase hydrolyzes ethyl butyrate into alcohol and butyric acid, and, further, that lipase is capable of effecting the synthesis of ethyl butyrate from butyric acid and ethyl alcohol; that is, the action of lipase is reversible. Baas[2] found that methyl, phenyl, and ethyl salicylates are hydrolyzed in the intestine of a dog. Schmiedeberg[3] showed that histozyme can hydrolyze hippuric acid into benzoic acid and glycocoll, and Niencki[4] showed that pancreas effects the same hydrolysis.

The triacetylglucose used in this work was made as follows:[5] Forty grams of crystallized glucose and 100 grams of acetic anhydride were mixed in a flask and heated to 100° C. Most of the glucose went into solution immediately, but an oil was left at the bottom. This was soon acted upon by the acetic anhydride, and so violently that the flask had to be cooled to avoid boiling over. Upon warming on the water-bath for three hours, the liquid had assumed a brownish color. This was poured into water in an evaporating dish, and was evaporated to a syrup, then diluted and again evaporated to a syrup. This syrup was shaken out with benzene in a separatory-funnel to extract a small amount of the triacetylglucose for analysis, and the residue was dissolved in 2 liters of water, and used in all the succeeding work. The benzene solution was evaporated to dryness and let stand in a desiccator over lime. The triacetylglucose remained behind as a thick oil with a faint smell of acetic acid. This oil was analyzed, and the analysis proved it to be triacetylglucose.

[1] This JOURNAL, **24**, 491.
[2] Ztschr. physiol. Chem., **14**, 416 (1890).
[3] Arch. f. exper. Path. u. Pharm., **14**, 379 (1881).
[4] *Ibid.*, **20**, 367 (1886).
[5] Schützenberger and Naudin : Bull. Soc. Chim., **12**, 204.

0.5186 gram substance gave 0.8945 gram CO_2 and 0.2743 gram H_2O.

	Calculated for $C_{12}H_{18}O_9$.	Found.
C	47.06	47.04
H	5.88	5.94

As this analysis would not show the composition of the main portion of the triacetylglucose, but only of that portion extracted with benzene, the 2 liters of triacetylglucose solution were analyzed as follows:

If the triacetylglucose (?) solution were treated with an alkali and boiled, the acetyl groups would be split off by hydrolysis and would neutralize part of the alkali; it should titrate as if it were N/3.30 acid. We titrated the boiling triacetylglucose solution against N/5 potassium hydroxide; when nearly neutralized the solution became slightly brown, so that the end of the titration could not be sharply detected. The results showed that the triacetylglucose solution was apparently N/3.44 acid; in other words, there seemed to be about 2.9 acetyl groups, instead of 3, to each glucose molecule. As this makes really no difference, as far as our problem is concerned, we shall use the expression "triacetylglucose solution," when speaking of the above solution.

	N/5 KOH solution. cc.	Triacetylglucose solution. cc.
1	13.00	8.86
2	17.24	11.71
3	20.64	14.39
4	28.04	19.42

Strength of triacetylglucose solution, N/3.44.

The main portion of the triacetylglucose, which was dissolved in the 2 liters of water, had a small amount of acetic acid in it. This amount was determined by titration with N/5 potassium hydroxide, using phenolphthalein as the indicator, this being the indicator used in all titrations.

	N/5 KOH solution. cc.	Triacetylglucose solution. cc.
1	0.67	5.56
2	0.90	7.08
3	1.00	8.47

Therefore, 1 cc. of the triacetylglucose solution equals 0.1218 cc. of the N/5 potassium hydroxide solution, or is N/41 in acid strength. This triacetylglucose solution was kept in an ice-box during all the work, and titrations of the acid strength were made from time to time. These titrations showed but little variation among themselves; in other words, triacetylglucose is not hydrolyzed to any appreciable extent by water at 0° C.

But a rise in temperature produces a very important change. As is well known, previous experiments by different men have all shown that in esterification or saponification reactions the rise in temperature increases the velocity of the change, but the amount of change is independent of the temperature. A solution of triacetylglucose that remained about N/42.50 for thirteen days, when kept at 0° C., was then kept at 37° C. An increase in the amount of hydrolysis was immediately noticeable, and the acidity in two days was N/35.7. We seem to have in triacetylglucose an exception to the above law. Whether the triacetylglucose is not hydrolyzed by water at 0° C., and is at 37° C., or whether the hydrolysis is so very slow at 0° C., that the acidity is practically unchanged in thirteen days, we cannot say at present.

The action of the enzymes, pancreatin, amylopsin, emulsin, maltase, diastase, takadiastase, etc., was tried. One hundred cc. of the triacetylglucose were treated with 0.5 gram to 1 gram of the enzyme to be studied, and were kept at a constant temperature of 0° C. Titrations were made at the beginning, and also every day or two, to determine the increase in the amount of acid present, and unless stated otherwise, the titrations of a given solution were made at the same time on each day; that is, exactly twenty-four hours, or a multiple of this time, apart. In some cases the enzyme itself has a slightly acid reaction, and the proper corrections have been made in the succeeding tables for this. In all cases studied, the enzyme hydrolyzed triacetylglucose into glucose and acetic acid. The amount of glucose present did not vary; that is, the enzyme did not use up any glucose. Some enzymes hydrolyzed only a small amount of the triacetylglucose, while

others effected relatively a large amount of hydrolysis. Pancreatin seemed to be the most active. Not only does pancreatin hydrolyze triacetylglucose, but it is also capable of effecting the union of acetic acid with glucose to form the glucose ester. Only a few experiments were carried out in this line, but these were carefully made and, together with the work of the previous paper, seem to prove that we are dealing here with a reversible action.

As most of the experiments were carried out at 0° C., we thought that it would be interesting to carry out some at 37° C. We find that the activity of pancreatin is greatly increased by a rise in temperature. As will be seen below, 0.5 gram of pancreatin in 100 cc. of triacetylglucose which, at 37° C., had become about constant at N/33 in acid strength, became N/26 in two days. The increase in acidity was N/123. One gram of pancreatin, or twice the above amount, in 100 cc. of triacetylglucose at 0° C. required two days to produce this increase in acidity ; pancreatin then showed twice as much activity at 37° as it did at 0°.

Many experiments show that in the hydrolysis of cane sugar, ethyl acetate, etc., by a given acid, the amount of hydrolysis is proportional to the amount of acid used. Experiments in which we used varying amounts of pancreatin in 100 cc. of triacetylglucose solution, showed that the amount of hydrolysis is dependent upon, and very nearly proportional to, the amount of enzyme present. The hydrolysis of the triacetylglucose is in no case complete. This does not necessarily show that the reaction is reversible, as the acetic acid produced would inhibit, to a certain extent, the action of the enzyme, and would finally cause the reaction to come to a standstill.

Experiment to Determine whether Glucose and Acetic Acid React at 0° or at 37°.—Twenty grams of recrystallized glucose melting at 147° and 5 cc. of glacial acetic acid were dissolved in 1 liter of water and titrated against N/5 potassium hydroxide solution, using phenolphthalein as indicator. The acid strength was N/11.70. After sterilizing at 120° for five minutes, the acid strength was N/11.51. The solution was kept

sterile in a flask with a siphon, so that portions of the liquid could be withdrawn without infecting the solution. Two days later the solution showed the same acid strength, N/11.51. Nine days later the acid strength had not changed, and the sterilized solution was then kept at a constant temperature of 37°. On the tenth day the acid strength was N/11.47, and on the fourteenth day was N/11.51. This shows that in a dilute solution of glucose and acetic acid there is no appreciable action and we need not consider this in our further work.

Experiment to Determine whether Pancreatin Acts upon Glucose in a Sterilized Solution.—A solution of 5 grams of pure glucose (melting at 147°) in 100 cc. of water was sterilized and cooled to 0° C. To this was added 0.5 gram of pancreatin that had been washed several times with absolute alcohol. To this solution was added a small amount of a mixture of thymol and toluene to keep the solution sterile. The mixture was thoroughly shaken and allowed to remain in the ice-chest a short time. Ten cc. were withdrawn by means of a sterilized pipette and titrated against N/5 potassium hydroxide, using phenolphthalein as indicator. One drop of the potassium hydroxide solution, or 0.03 cc., was enough to produce a decided pink color. The solution was allowed to remain in the ice-box four days, but no change was visible. No gas was given off, showing that no fermentation had taken place. At the end of the fourth day 10 cc. of the solution were removed, as before, and titrated. One drop, or 0.03 cc., of the potassium hydroxide solution was again sufficient to produce a decided pink color. Enzymes do not ferment sugars, and in our further experiments upon the action of enzymes on triacetylglucose we are sure that there is no formation of acid from part of the glucose formed by the hydrolysis of the triacetylglucose.

Experiment to Determine whether Pancreatin in Sterilized Water Decomposes and Forms an Acid or Alkaline Solution.—One-half gram of pancreatin was added to 100 cc. of distilled water and 1 cc. of toluene was added. The solution was kept

at 0° C. It was slightly acid, as the following titrations show :

Titration at the Beginning.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
0.12	5.00	
0.17	7.00	N/207

Titration after Forty-eight Hours.

0.11	5.00	
0.24	10.00	N/215

The acid strength of the pancreatin solution is N/215, a hardly perceptible change from the above. In further experiments, then, we can disregard the decomposition of the enzyme itself.

Triacetylglucose Solution.—As stated above, this stock solution was kept sterile by means of toluene and thymol, and was kept in an ice-box. Titrations were made from time to time to see if any hydrolysis could be detected. As seen from the tables there was no appreciable change in the acid strength, and no fermentation was ever noticed.

Titration at the Beginning.

N/4 potassium hydroxide solution. cc.	Triacetylglucose solution. cc.	Acidity.
0.60	5.09	
0.75	6.37	
0.95	7.95	N/42.45

Titration after Twenty-four Hours.

0.59	5.03	
0.89	7.34	
1.04	8.60	N/41.85

Titration after Forty-eight Hours.

0.60	5.09	
0.88	7.14	
1.11	8.83	N/40.65

Titration after One Hundred and Twenty Hours.

0.58	5.00	
0.86	7.00	N/42

Titration after One Hundred and Forty-four Hours.

N/5 potassium hydroxide solution. cc.	Triacetylglucose solution. cc.	Acidity.
0.57	5.00	
0.85	7.00	N/42.50

Other titrations were made after this time but no appreciable change was noticed.

Experiment to Determine the Change in a Solution of Triacetylglucose by Raising the Temperature from 0° to 37°.—As we expected to carry out experiments in which the solution of triacetylglucose would be subjected to a change in temperature from 0° to 37°, it was thought necessary to determine whether this solution itself would change in acid strength upon heating. A sterilized solution of triacetylglucose was titrated and then put into an oven having a constant temperature of 37°. As will be seen from the tables, the amount of hydrolysis was increased by a rise in temperature.

Titration at the Beginning.

N/5 potassium hydroxide solution. cc.	Triacetylglucose solution. cc.	Acidity.
0.60	5.00	
0.86	7.00	N/41

Titration after Twenty-four Hours.

0.66	5.00	
0.95	7.00	N/37.5

Titration after Forty-eight Hours.

0.70	5.00	
1.41	10.00	N/35.7

In two days the acidity of the triacetylglucose solution increased from N/41 to N/35.7. As will be seen below, this solution finally became constant at about N/33.

Hydrolysis of Triacetylglucose by Pancreatin.—A solution of 1 gram of pancreatin in 100 cc. of the above solution of triacetylglucose was made, and the acid strength was determined by titration to be N/40.65. This, as were all of the other solutions, was kept sterile by means of toluene and thymol and was kept at constant temperature of 0°.

Titration after Forty-eight Hours.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
1.15	7.19	
1.42	8.71	
1.85	11.10	N/30.64

Titration after Ninety-six Hours.

1.00	5.00	
1.49	7.00	N/24.25

Titration after Two Hundred and Forty Hours.

.1.18	5.00	
1.62	7.00	N/21

Hydrolysis of Triacetylglucose by Amylopsin.—One gram of amylopsin was dissolved in 100 cc. of triacetylglucose solution and kept sterile by means of toluene. The acidity at first was N/41.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution. cc.	Amylopsin solution. cc.	Acidity.
0.70	4.95	
1.02	7.15	
1.28	8.95	N/35.10

Titration after Ninety-six Hours.

0.80	5.00	
1.20	7.00	N/30.20

Titration after Two Hundred and Forty Hours.

1.00	5.00	
1.40	7.00	N/25

Hydrolysis of Triacetylglucose by Emulsin.—This solution was made by adding 1 gram of emulsin to 100 cc. of the solution of triacetylglucose, and was kept sterile by means of thymol and toluene. It titrated N/50 acid at first.

see errata V. 29 p. 88.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution. cc.	Emulsin solution. cc.	Acidity.
0.75	6.01	
1.05	8.25	
1.20	9.72	N/39.93

Titration after Ninety-six Hours.

0.60	5.00	
0.88	7.00	N/40.40

Titration after Two Hundred and Sixty-four Hours.

0.62	5.00	
0.87	7.00	N/40.50

We see that emulsin hardly hydrolyzes triacetylglucose even in ten days.

Hydrolysis of Triacetylglucose by Maltase.—Fresh malt was powdered and sifted and 4 grams added to 100 cc. of the solution of triacetylglucose. This was kept sterile in an ice-box. The solution was N/42.44 at first.

Titration after Forty-eight Hours.

N/5 potassium hydroxide solution. cc.	Maltase solution. cc.	Acidity.
0.69	4.62	
0.97	6.64	
1.20	8.24	N/34

Titration after Seventy-two Hours.

0.79	5.24	
1.10	7.33	
1.49	10.02	N/33.35

Titration after Ninety-six Hours.

0.93	5.37	
1.11	6.52	
1.35	8.00	N/29.30

Titration after One Hundred and Sixty-eight Hours.

0.95	5.00	
1.39	7.00	N/25.75

Titration after Three Hundred and Thirty-six Hours.

1.13	5.00	
1.57	7.00	N/22.20

Hydrolysis of Triacetylglucose by Diastase.—This solution was made by adding 2 grams of diastase to 100 cc. of the solution of triacetylglucose, and was kept sterile by means of thymol. The temperature was kept at 0° C. The acidity at first was N/40.90, as shown by the tables.

Titration of Fresh Solution.

N/5 potassium hydroxide solution. cc.	Diastase solution. cc.	Acidity.
0.63	5.10	
0.91	7.55	
1.19	9.70	N/40.90

Titration after Twenty-four Hours.

0.96	7.60	
1.55	12.15	
2.05	16.15	N/39.39

Titration after Forty-eight Hours.

0.70	5.38	
0.90	6.93	
1.11	8.45	N/38.62

Titration after One Hundred and Twenty Hours.

0.66	5.00	
0.98	7.00	N/37.8

Titration after Two Hundred and Eighty-eight Hours.

0.71	5.00	
1.01	7.00	N/35

Hydrolysis of Triacetylglucose by Takadiastase.—This solution was made by adding 0.5 gram of takadiastase to 100 cc. of the solution of triacetylglucose . It was kept in an icebox. The acid strength was N/41.

Titration after Twenty-four Hours.

N/5 potassium hydroxide solution. cc.	Takadiastase solution. cc.	Acidity.
0.76	5.00	
1.10	7.00	N/32.35

Titration after Ninety-six Hours.

0.87	5.00	
1.19	7.00	N/29

Titration after One Hundred and Sixty-eight Hours.

N/5 potassium hydroxide solution. cc.	Takadiastase solution. cc.	Acidity.
0.93	5.00	
1.32	7.00	N/27

Effect of Rise in Temperature on the Amount of Hydrolysis by Pancreatin.—One-half gram of pancreatin was added to 100 cc. of a solution of triacetylglucose that had been kept at 37° for some time, and that had become constant at about N/33. This solution was kept sterile by means of toluene and was kept at a constant temperature of 37°.

Titration at First.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
0.74	5.00	
1.08	7.00	N/33

Titration after Twenty-four Hours.

0.89	5.00	
1.22	7.00	N/28

Titration after Forty-eight Hours.

0.98	5.00	
1.89	10.00	N/26

As the table shows, the increase in acidity in forty-eight hours was N/123, which is approximately the increase produced by 1 gram of pancreatin, or twice the amount here used, in the same volume of the cold solution in the same time. The activity of pancreatin, then, is approximately twice as great at 37° as it is at 0°.

Experiments to Determine the Relation between the Amount of Pancreatin Used and the Amount of Hydrolysis.—Three solutions were made containing 0.25 gram, 0.5 gram, and 0.75 gram, respectively, of pancreatin in 100 cc. of the solution of triacetylglucose. These were kept at 0° and were sterilized by means of toluene. As the tables show, the amount of hydrolysis is approximately proportional to the amount of enzyme used. The tables show the amount of acetic acid

formed in one liter. The solutions were all approximately N/41 at first.

Titration after Forty-eight Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.	Acetic acid formed in 1 liter. Gram.
0.69	5.00		
0.96	7.00	N/36	0.20

With solution containing 0.5 gram pancreatin.

| 0.77 | 5.00 | | |
| 1.11 | 7.00 | N/32 | 0.41 |

With solution containing 0.75 gram pancreatin.

| 0.83 | 5.00 | | |
| 1.18 | 7.00 | N/29.5 | 0.57 |

As can be seen, the figures 0.20, 0.41, and 0.57 gram are very nearly in the ratios 1 : 2 : 3.

Titration after Ninety-six Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.	Acetic acid formed in 1 liter. Gram.
0.68	5.00		
0.97	7.00	N/36.5	0.18

With solution containing 0.5 gram pancreatin.

| 0.79 | 5.00 | | |
| 1.10 | 7.00 | N/32 | 0.42 |

With solution containing 0.75 gram pancreatin.

| 0.87 | 5.00 | N/29 | 0.60 |
| 1.19 | 7.00 | N/28 | 0.58 |

Here again, the ratios of the amounts of acid generated are approximately the same as the ratios of the amounts of pancreatin used.

Titration after One Hundred and Forty-four Hours.

With solution containing 0.25 gram pancreatin.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.	Acetic acid formed in 1 liter. Gram.
0.72	5.00		
0.99	7.00	N/35	0.25

With solution containing 0.5 gram pancreatin.

0.83	5.00		
1.18	7.00	N/30	0.54

With solution containing 0.75 gram pancreatin.

0.91	5.00		
1.25	7.00	N/27.5	0.72

As will be seen from the above tables, the amount of triacetylglucose hydrolyzed is very nearly proportional to the amount of pancreatin present.

Experiment to Determine whether Pancreatin Can Cause Esterification in a Mixture of Glucose and Acetic Acid.—Twenty grams of glucose (melting-point 147°) and 5 cc. of glacial acetic acid were dissolved in 1 liter of water. Fifty cc. of this solution were diluted to 200 cc., and to this solution were added 0.5 gram of pancreatin and 2 cc. of toluene. The solution was kept at 0°.

Titration at First.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
0.68 *see errata* V.29 p.88 0.67	5.00	N/37.35

Titration after Twenty-four Hours.

0.66	5.00	
0.93	7.00	N/37.75

Titration after Seventy-two Hours.

0.63	5.00	
0.89	7.00	*see errata*
1.52	12.00	V.29 N/39.50

Titration after Ninety-six Hours.

0.62	5.00	
0.88	7.00	
1.51	12.00	N/40

Titration after One Hundred and Twenty Hours.

N/5 potassium hydroxide solution. cc.	Pancreatin solution. cc.	Acidity.
0.63	5.00	
1.25	10.00	N/40

As the tables show, the acidity decreased from N/37.35 to N/40. When the acidity had decreased to N/40 we noticed that the pink color of the solution that had been titrated would nearly disappear after a short time, indicating the presence of glucose acetates, which were slowly saponified by the potassium hydroxide. As the decrease in acidity in this experiment is only a very small amount, we do not think this decisive. We are therefore carrying out other experiments to determine this point more carefully. But when these results are taken in connection with the previous paper, in which it was clearly shown that such esters were formed by bacteria, it is very probable that further experiments will show decisively that enzymes can form glucose acetates from, as well as hydrolyze them into, glucose and acetic acid. The work has been unavoidably interfered with, but we shall now take it up again, and the above is intended as a preliminary announcement.

CHICAGO, July 15, 1902.

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RING CONDENSATIONS OF THE ESTERS OF URA-MIDO AND SEMICARBAZINO ACIDS WITH SODIUM ALCOHOLATE.

BY J. R. BAILEY.

INTRODUCTION.

In an investigation of the ethyl ester of hydantoic acid[1] the author, in connection with C. P. Norby, discovered that this substance, when treated with sodium or potassium alcoholate, readily passes into the sodium or potassium salt, respectively, of hydantoin. Further investigation has shown that sodium

[1] The work on this substance was finished when Harries reported its discovery and its conversion into hydantoin by means of hydrochloric acid (Ber. d. chem. Ges., **33**, 3418). The publication of this work has been deferred until now, owing to the withdrawal of Mr. Norby from the University and a year's absence of the author.

alcoholate can be employed as a general reagent to effect ring condensations with the esters of both uramido and semicarbazino acids. This use of sodium alcoholate may be regarded as an extension of Michael's method for the preparation of cyclical ureides.[1] The experiments herein described weer carried out for the most part in each case with not more than I or 2 grams of substance and were seldom repeated. The yields when given are, therefore, not to be regarded as the maximum yields to be obtained in working with large quantities of material. Our efforts were rather directed toward establishing the general applicability of the reaction. As the reaction takes place in the cold, and as in none of the condensations a by-product is obtained, this reaction, where applicable, may be considered as giving an almost quantitative yield.

All attempts to split off alcohol from the ethyl ester of the semicarbazone of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_2H_5,$$
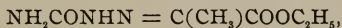
were futile. This is rather peculiar, in view of the fact that the ethyl ester of semicarbazinopropionic acid readily passes into the corresponding dihydromethyldioxy-α-triazine. This latter condensation takes place especially readily with sodium alcoholate thus :

$$NH_2CONHNHCH(CH_3)COOC_2H_5 \quad \rightarrow$$
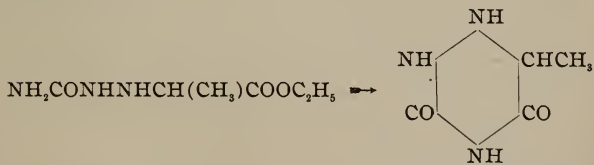
(In form of sodium salt.)

The ethyl ester of semicarbazinopyruvic acid[2] can be obtained by oxidizing the ethyl ester of semicarbazinopropionic acid, and differs from it in having two hydrogen atoms less. Furthermore, the methyldioxy-α-triazine sought is easily obtained by oxidizing the dihydrotriazine referred to above.[3]

[1] *J. prakt. Chem.*, [2] **35**, 456.
[2] *Ann. Chem.* (Liebig), **303**, 87.
[3] *Ibid.*, p. 82.

Thiele and Dralle report similar failures to effect triazine condensations in the hydrazone series.[1] It would be interesting to know the action of sodium alcoholate on the oxidation-product of the ethyl ester of semicarbazino-iso-butyric acid but, because of lack of material, this part of the investigation has been deferred. Here the oxidation-product would not be a semicarbazone but an azo compound,

$$NH_2CON = NC(CH_3)_2COOC_2H_5,$$
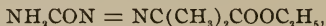
with two hydrogen atoms less than the corresponding hydrazo compound.

The behavior of the benzoyl derivative of the ethyl ester of semicarbazinopropionic acid,

$$NH_2CONHN(COC_6H_5)CH(CH_3)COOC_2H_5,$$
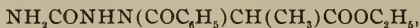
towards sodium alcoholate was investigated to see whether a triazol condensation with the elimination of water, or a triazine condensation with the elimination of alcohol would be effected. The reaction goes normally with the formation of a benzoyltriazine. The benzoyl derivative thus obtained can, however, by the action of an aqueous alkali, be converted into 3-oxy-5-phenyltriazol-1-propionic acid :
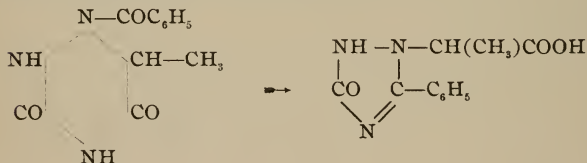
This reaction, which might at first seem rather peculiar, can be very easily interpreted as follows : The alkali splits the triazine ring forming the alkali salt of benzoylsemicarbazinopropionic acid, and, as Bailey and Acree showed, this latter substance, under the influence of an alkali, passes with the elimination of water into 3-oxy-5-phenyltriazol-1-propionic acid.[2]

The behavior of the ethyl ester of semicarbazinopropionic

[1] Ann. Chem. (Liebig), **302**, 275.
   Ber. d. chem. Ges., **33**, 1525.

acid toward alcoholic potash is of considerable theoretical interest. When to this ester, in absolute alcohol, alcoholic potash is added, there begins, after a few minutes, a separation of dihydromethyldioxy-α-triazine. The normal action of alcoholic potash on an ester is saponification, but its action here is to effect a ring condensation by splitting off alcohol. This reaction is all the more peculiar in that there is no salt formed by the triazine and the potash, and because, furthermore, the triazine here formed, which is a cyclical amide, is very unstable toward aqueous alkalies, being hydrolyzed on treatment with 0.5 molecule of barium hydroxide to semicarbazinopropionic acid, thus:

$$\text{NH} \quad \text{CO} \quad \text{CH—CH}_3 \quad \text{NH} \quad \text{NH} \quad \text{CO} \quad \longrightarrow \quad \text{NH}_2\text{CONHNHCH(CH}_3\text{)COOH}$$
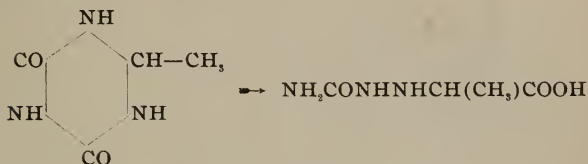
It was of interest to determine whether the ethyl ester of hydantoic acid would undergo a similar condensation with alcoholic potash to hydantoin, and it was found that the normal reaction of saponification takes place.

A very satisfactory modification of Fischer's method of esterification was used in the case of hydantoic acid and the two semicarbazino acids worked with. These substances are very sensitive toward mineral acids, and in the case of hydantoic acid, where even as dilute a solution of hydrochloric acid in alcohol as 3 per cent was used, it was found that if the solution were boiled all of the substance to be esterified was converted into hydantoin. However, if hydantoic acid or the semicarbazino acids are allowed to stand with 3 per cent alcoholic hydrochloric acid two weeks, esterification, without ring condensation, is effected. This method of esterification is especially welcome in the series of semicarbazino fatty acids, where in some cases all attempts to prepare the esters from the nitrils, with the imido

ethers as intermediary products, have been unsuccessful ; for example, the methylimido ether of semicarbazinopropionic acid was not obtained by the action of alcoholic hydrochloric acid or alcoholic sulphuric acid on the nitril, although these methods give the corresponding ethyl and propyl imido ethers. Repeated attempts to prepare esters of semicarbazinoisobutyric acid by the action of alcoholic solutions of acids on the nitril of semicarbazinoisobutyric acid gave in no case even a trace of the ester.

EXPERIMENTAL PART.

I.

Condensation of the Esters of Uramido Acids to Hydantoins.[1]

The Ethyl Ester of Hydantoic Acid.—This substance is best prepared according to the method of Harries referred to above, but it may also be prepared by the esterification of hydantoic acid : Ten grams of hydantoic acid were put into 240 cc. of alcoholic hydrochloric acid, whereupon, after a few minutes' shaking, complete solution was effected. After standing two weeks in the cold, the solution was neutralized with sodium bicarbonate and the alcohol removed by evaporation. The residue, when extracted with alcohol, yielded 12.37 grams of ester, or 97 per cent of the theoretical. In an experiment in which hydantoic acid in 3 per cent alcoholic hydrochloric acid was boiled for several hours, all of the acid was converted into hydantoin. The latter substance was identified by its solubility and melting-point, and by a nitrogen determination.

0.0923 gram substance gave 22.9 cc. N at 18° and 750 mm.

	Calculated for $C_3H_4O_2N_2$.	Found.
N	28.00	28.27

The ethyl ester of hydantoic acid gives, with sodium or potassium alcoholate, the corresponding salt of hydantoin. However, unlike the ethyl ester of semicarbazinopropionic acid, it reacts normally with alcoholic potash, giving the

[1] The investigation of the hydantoic acid derivatives and hydantoin was carried out conjointly with C. P. Norby.

potassium salt of hydantoic acid.[1] This salt decomposes at about 130°.

0.1878 gram substance gave 0.1040 gram K_2SO_4.

	Calculated for $C_3H_5O_3N_2K$.	Found.
K	25.00	24.82

The amide of hydantoic acid can be prepared by allowing the ester to stand with alcoholic ammonia. It melts with evolution of gas at 204°.

0.1340 gram substance gave 0.1515 gram CO_2 and 0.0735 gram H_2O.

0.1391 gram substance gave 42.4 cc. N at 12° and 756 mm.

	Calculated for $C_3H_7O_2N_3$	Found.
C	30.77	30.83
H	5.98	6.09
N	35.90	35.99

The nitril of hydantoic acid[2] can be obtained by bringing together in concentrated aqueous solutions potassium cyanate and the nitril of glycocoll hydrochloride in molecular proportions.[3] It crystallizes from water in prisms, which melt at 139° to a clear liquid, and, on boiling in aqueous solution with 0.5 molecule of barium hydroxide, is saponified to hydantoic acid.

0.1628 gram substance gave 59.5 cc. N at 13° and 752.5 mm.

	Calculated for $C_3H_5ON_3$.	Found.
N	42.42	42.76

Salts of Hydantoin.—When concentrated solutions of sodium alcoholate and the ethyl ester of hydantoic acid in molecular proportion are mixed, the sodium salt of hydantoin immediately separates as a fine, pulverulent precipitate. After being washed with alcohol and ether, and dried at 110° for several hours, the salt is sufficiently pure for analysis. The substance is only sparingly soluble in alcohol and, although

[1] Ann. Chem. (Liebig), **136**, 281.

[2] This work was completed when Klages announced the method of preparation of this substance. However, he gives no analytical data or properties of the substance in proof of its constitution (J. prakt. Chem., [2], **65**, 188).

[3] Ber. d. chem. Ges., **27**, 59.

readily soluble in water, probably with hydrolysis, does not deliquesce in the air. Two grams of ester gave 2.06 grams of the air-dried sodium salt of hydantoin; the theoretical yield for $NaC_3H_3O_2N_2$ is 1.67 grams. This yield indicates that the initial reaction-product may possibly be constituted as follows:

$$OC \begin{array}{c} \diagup NH-CH_2 \\ \quad | \quad \diagup ONa \\ \diagdown NH-C-OC_2H_5 \end{array} .$$
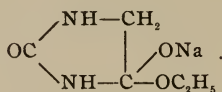
And that this, on heating, or more slowly *in vacuo*, splits off alcohol, giving

$$CO \begin{array}{c} \diagup NH-CH_2 \\ \quad | \\ \diagdown N=C-ONa \end{array} .$$
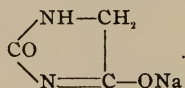
The first analyses of the sodium salt made were carried out with a sample that was allowed to stand *in vacuo* several days over sulphuric acid and it gave results too low for the simple sodium salt of hydantoin and too high for this salt plus 1 molecule of alcohol. Analysis of sample dried *in vacuo*.

0.1858 gram substance gave 32.1 cc. N at 12°.5 and 754 mm.
0.2201 gram substance gave 0.1108 gram Na_2SO_4.

	Calculated for $C_3H_3O_2N_2Na + C_2H_6O$.	Found.
N	16.67	20.30
Na	13.69	16.31

Analysis of sample dried at 110° for four hours:
0.1211 gram substance gave 23.9 cc. N at 12° and 748 mm.
0.2371 gram substance gave 0.1380 gram Na_2SO_4.

	Calculated for $C_3H_3O_2N_2Na$.	Found.
N	22.95	23.05
Na	18.85	18.88

The constitution of the salts of hydantoin will be further investigated and the results announced later.

The potassium salt can be obtained in the same way as the sodium salt by the action of potassium alcoholate on the ethyl

ester of hydantoic acid. For the analysis the sample was dried at 110°.

0.2670 gram substance gave 45.3 cc. N at 12° and 754 mm.
0.1483 gram substance gave 26.1 cc. N at 16° and 746 mm.
0.2666 gram substance gave 0.1681 gram K_2SO_4.

	Calculated for $C_3H_3O_2N_2K$.	I.	Found. II.
N	20.29	19.98	20.13
K	28.26	28.26	. . . .

Hydantoin can be prepared from its sodium or potassium salt by making concentrated aqueous solutions of the latter slightly acid with hydrochloric acid. Hydantoin prepared in this way proved to be identical with a sample prepared according to the method of Harries. Harries' method of preparation is, however, to be preferred, as it allows a direct and almost quantitative conversion of the ethyl ester of hydantoic acid into hydantoin without the formation of any inorganic by-products. In working with small quantities of substance, the yield of hydantoin by the sodium alcoholate method is about 80 per cent of the theoretical. A sample of hydantoin obtained by this method gave the following results on analysis :

0.2832 gram substance gave 0.3735 gram CO_2 and 0.1027 gram H_2O.

0.1174 gram substance gave 28.5 cc. N at 16°.5 and 760 mm.

	Calculated for $C_3H_4O_2N_2$.	Found.
C	36.00	35.97
H	4.00	4.03
N	28.00	28.24

The Ethyl Ester of Lacturaminic Acid,

$NH_2CONHCH(CH_3)COOC_2H_5$.—This ester can be prepared similarly to the ester of hydantoic acid, by treatment of the hydrochloride of the ethyl ester of alanine with potassium cyanate. It is readily soluble in water, chloroform, and alcohol ; difficultly soluble in ether and petroleum ether. The substance is best purified by crystallization from benzene. It is thus obtained in the form of a matted mass of very slen-

der, short needles, as seen under the microscope, and melts at 100° to a clear liquid.

0.1692 gram substance gave 27.6 cc. N at 24°.5 and 749 mm.

0.1834 gram substance gave 29.8 cc. N at 25° and 746 mm.

0.2946 gram substance gave 0.4838 gram CO_2 and 0.1982 gram H_2O.

	Calculated for $C_6H_{12}O_3N_2$.	Found.	
		I.	II.
C	45.00	44.79	....
H	7.50	7.47	....
N	17.50	17.97	17.78

The ethyl ester of lacturaminic acid, when treated in alcoholic solution with sodium alcoholate, passes into the sodium salt of lactylurea. As both the sodium and potassium salts separate as a gelatinous mass, difficult to filter, they were not isolated. The method employed in the preparation of lactylurea can be used to advantage where it is not desired to isolate the salt of the alcoholate condensation-product. The reaction-product of the alcoholate and the ester is poured into a very little water, kept slightly acid with hydrochloric acid, and, after neutralization of the alcoholate, the excess of hydrochloric acid is neutralized with ammonia. The solution is then evaporated and the residue extracted with any suitable solvent, usually alcohol. By this method a yield of about 85 per cent of lactylurea can be obtained from the ethyl ester of lacturaminic acid. Prepared in this way, the substance has the properties given by Heinz.[1] Crystallized from alcohol, containing 15 per cent of ether, lactylurea melts at 148°, whereas Heinz gives 140° as the melting-point of the substance crystallized from water.

0.1977 gram substance gave 44.6 cc. N at 25° and 750 mm.

	Calculated for $C_4H_6O_2N_2$.	Found.
N	24.56	24.83

The Ethyl Ester of γ-Phenylhydantoic Acid,

$C_6H_5NHCONHCH_2COOC_2H_5$.—Two grams of the ethyl ester of glycocoll hydrochloride and 1.28 grams of sodium bicarbonate are dissolved in 25 cc. of ice-water and then 1.78 grams of

[1] Ann. Chem. (Liebig), **169**, 124.

phenyl isocyanate added. In order to thoroughly emulsify the isocyanate, the mixture is shaken vigorously, when, after a few minutes, the ester of phenylhydantoic acid separates out. Two grams of the ester of glycine hydrochloride gave 2.6 grams of the ester of phenylhydantoic acid. The ester can be purified by crystallization from dilute alcohol or benzene. It crystallizes in slender needles that melt to a clear liquid at 108° to 109°.

0.2342 gram substance gave 27.7 cc. N at 27° and 748 mm.

0.2938 gram substance gave 0.6452 gram CO_2 and 0.1669 gram H_2O.

	Calculated for $C_{11}H_{14}O_3N_2$.	Found.
C	59.46	59.89
H	6.31	6.31
N	12.61	12.84

The ethyl ester of γ-phenylhydantoic acid reacts with sodium alcoholate giving γ-phenylhydantoin, a substance described by Guareschi.[1] The sodium salt, if formed here, is soluble in alcohol and the hydantoin must be isolated by the method described under lactylurea. The hydantoin prepared in this way was compared with some made according to the method of Guareschi and the two samples proved to be in every respect identical.

0.2426 gram substance gave 36.2 cc. N at 28° and 746 mm.

	Calculated for $C_9H_8O_2N_2$.	Found.
N	15.91	16.08

γ-Phenylhydantoic acid can be made from γ-phenylhydantoin by boiling the latter for a few minutes with a barium hydroxide solution. On acidifying the solution the acid separates out and can be purified by crystallization from alcohol. It crystallizes in short, slender needles, that melt with evolution of gas at 197°.

0.1393 gram substance gave 18.8 cc. N at 28° and 751 mm.

	Calculated for $C_9H_{10}O_3N_2$.	Found.
N	14.43	14.64

[1] Beilstein, Vol. II., p. 383.

II.

Condensation of the Esters of Semicarbazino Acids to Triazines.

The semicarbazinopropionitril,

$$NH_2CONHNHCH(CH_3)CN,$$
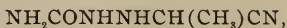
used in this work was prepared according to the method of Thiele and Bailey[1] with the following modifications : Almost absolute prussic acid was used instead of a 60 per cent solution, and to every 500 cc. were added 2 cc. of strong hydrochloric acid. The first modification has the advantage that the nitril can be much more readily isolated than when a dilute prussic acid is employed, and the second modification prevents the prussic acid from polymerizing.

The semicarbazinopropionic acid[2] used in our experiments was prepared by saponifying semicarbazinopropionitril with barium hydroxide.[3] In this method of preparation the nitril is allowed to stand one week, dissolved in twenty-five times its weight of water, with 0.5 molecule of barium hydroxide, in order to effect a conversion of the nitril into the amide, and then the solution is boiled until the smell of ammonia disappears. After the removal of the barium as sulphate the solution is evaporated to a small bulk and the acid allowed to crystallize out. Certain modifications of this process, looking toward a better yield, are now being tried and will be published later.

The following modification of the process of Thiele and Bailey[4] was employed in the preparation of the ethyl ester of semicarbazinopropionic acid : Thirty-eight grams of nitril were put into 150 cc. of absolute alcohol and saturated with hydrochloric acid gas at 0°. In order to keep the alcohol constantly stirred, and at the same time exclude moisture, the delivery tube for the gas was provided on its lower end with a Witt stirrer, and the flask containing the nitril, as well as the gas exit from the hydrochloric acid generator, were provided with mercury seals constructed so as to keep moisture out of

[1] Ann. Chem. (Liebig), **303,** 80.

[2] *Ibid.,* p. 84.

[3] This method of preparation was worked out conjointly with S. F. Acree.

[4] Ann. Chem. (Liebig), **303,** 83.

the alcohol and allow a free rotation of the stirrer. Despite these precautions and the fact that after saturation the alcoholic solution was cooled to —25° for two hours, the imido ether did not separate out. After the solution had stood twenty-four hours the alcohol was distilled off *in vacuo* (bath at 60°), the residue taken up with a little water, and ammonia added to neutralization. The solution was now repeatedly shaken out with chloroform as long as any ester was obtained. The chloroform extracts yielded 24.7 grams of ester, or about 47 per cent of the theoretical. From the aqueous solution there separated out 2.8 grams of dihydromethyl-dioxy-α-triazine, or about 7 per cent of the theoretical. Sulphuric acid can be substituted for hydrochloric acid in the preparation of this ester, but thus far this method has not given so good a yield as does the hydrochloric acid method.

The Propyl Ester of Semicarbazinopropionic Acid.—This ester was prepared, similarly to the ethyl ester, by the action of propyl alcohol and hydrochloric acid on the nitril. Seven grams of nitril gave 3.5 grams of pure propyl ester. This ester is very soluble in alcohol and water, difficultly soluble in benzene, and very difficultly soluble in ether. It is best crystallized from benzene or acetic ether. From a solution of the latter it crystallizes, on evaporation, in long slender needles, which melt at 89° to a clear liquid.

0.2766 gram substance gave 0.4552 gram CO_2 and 0.2024 gram H_2O.

0.1586 gram substance gave 31 cc. N at 14° and 750 mm.

0.1598 gram substance gave 31.4 cc. N at 17° and 751 mm.

	Calculated for $C_7H_{15}O_3N_3$.	I.	Found. II.
C	44.44	44.88	. . . .
H	7.95	8.13	. . . .
N	22.22	22.69	22.53

The propyl ester, treated with potassium permanganate in dilute sulphuric acid solution, gives the corresponding ester of the semicarbazone of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_3H_7,$$
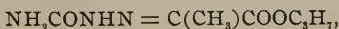
a substance which separates out of very dilute solutions. It melts at 178° to a clear liquid.

0.1434 gram substance gave 27.9 cc. N at 17° and 756 mm.

	Calculated for $C_7H_{18}O_3N_3$.	Found.
N	22.47	22.46

The Methyl Ester of Semicarbazinopropionic Acid.--Five grams of semicarbazinopropionic acid were allowed to stand four days with 120 cc. of a 3 per cent solution of hydrochloric acid in methyl alcohol. After neutralization with ammonium hydroxide the solution was evaporated to a small bulk and then extracted with chloroform. Yield 3.1 gram. No attempt was made to regain the unesterified acid. For the analysis the ester was crystallized from benzene, in which it is difficultly soluble, then from alcohol. From benzene it crystallizes in radiating bundles of slender prisms that melt at 100° to a clear liquid. With potassium permanganate in dilute sulphuric acid, the ester gives a semicarbazone which melts with decomposition at 208°.

0.1412 gram substance gave 34.4 cc. N at 27°.5 and 748 mm.
0.2377 gram substance gave 0.3248 gram CO_2 and 0.1476 gram H_2O.

	Calculated for $C_5H_{11}O_3N_3$.	Found.
C	37.27	37.27
H	6.83	6.90
N	26.09	26.31

Preparation of 3,5-Dioxy-6-methyl-1,6-dihydro-1,2,4-triazine,[1]
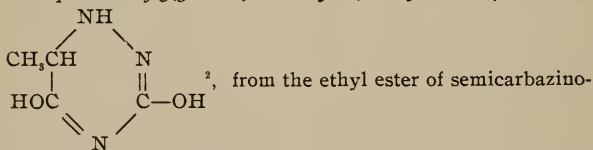
$$
\begin{array}{c}
\text{NH} \\
\diagup \quad \diagdown \\
\text{CH}_3\text{CH} \quad \quad \text{N} \\
| \quad\quad\quad \| \\
\text{HOC} \quad\quad \text{C—OH} \\
\diagdown \quad \diagup \\
\text{N}
\end{array}
$$[2], from the ethyl ester of semicarbazino-

propionic acid. The condensation of the ester to the triazine may be effected in four ways : (1) by the action of mineral

[1] It is not intended by this formula to distinguish between the several tautomeric possibilities.

[2] For the sake of brevity this substance will be referred to as triazine.

acids ;[1] (2) by heat ; (3) by alcoholic potash ; (4) by sodium alcoholate.

Two grams of the ester were heated for three hours at 120°. There was obtained from the fusion 0.5 gram of triazine, which was identified by its melting-point and solubilities.

To 10 grams of the ethyl ester in 25 cc. of methyl alcohol were added 12 cc. of a solution of caustic potash in absolute methyl alcohol. After three hours' standing, 5.4 grams of triazine had separated out. The filtrate, when neutralized with acetic acid, yielded 1.7 grams of triazine, making in all a yield equal to 83 per cent of the theoretical. As yet, semicarbazinopropionic acid has not been detected as one of the reaction-products here. The methyl and propyl esters are also converted into triazine by alcoholic potash.

If to 1 molecule of the ester, dissolved in the least amount of alcohol, there be added 1 molecule of sodium alcoholate in concentrated alcoholic solution, an immediate precipitation of the sodium salt of the triazine takes place. For the analysis the salt was filtered off, boiled with alcohol, washed with alcohol and finally with ether, and then dried for four hours at 110°. This triazine salt, unlike the corresponding salt of hydantoin, is very hygroscopic.

0.1656 gram substance gave 42.4 cc. N at 29° and 749 mm.
0.5150 gram substance gave 0.2362 gram Na_2SO_4.

	Calculated for $C_4H_6O_2N_3Na$.	Found.
N	27.81	27.56
Na	15.23	14.87

Five grams of the ester gave 3.28 grams of triazine, or about 89 per cent of the theoretical yield.

Action of Barium Hydroxide on the Triazine.—The triazine, on boiling with a barium hydroxide solution containing 2.4 grams of barium hydroxide to 1 gram of the triazine, for one-half hour, is changed into semicarbazinopropionic acid. One gram of triazine yielded 0.62 gram of pure acid, which proved identical with the acid obtained from semicarbazinopropionitril.

[1] Ann. Chem. (Liebig), **303**, 81.

0.2765 gram substance gave 68 cc. N at 13° and 751 mm.

	Calculated for $C_4H_9O_3N_3$.	Found.
N	28.57	28.72

3,5-Dioxy-6-methyl-1-benzoyl-1,6-dihydro-1,2,4-triazine—The ethyl ester of benzoylsemicarbazinopropionic acid,[1] treated in the usual way with sodium alcoholate, is converted into benzoyltriazine. The sodium salt does not separate out, but the benzoyltriazine can be isolated by the method given under lactylurea. It is readily soluble in hot alcohol, from which it crystallizes in short, microscopic prisms. This substance melts at 201° to a clear liquid, beginning to soften a few degrees below that point. After melting, it solidifies at about 180°, and then has a melting-point of 210°. This modification that melts at 210°, which is probably a tautomeric form, represents the labile form, as, on being crystallized from alcohol, it shows the same melting-point peculiarities as the original benzoyl derivative. Both before and after fusion the benzoyl triazine gives a deep reddish-brown color with an alcoholic solution of ferric chloride.

0.2436 gram substance gave 0.5057 gram CO_2 and 0.1052 gram H_2O.

	Calculated for $C_{11}H_{11}O_3N_3$.	Found.
C	56.65	56.62
H	4.72	4.80

The benzoyltriazine, on being heated with 10 per cent potassium hydroxide solution for a few minutes, is changed into 3-oxy-5-phenyltriazole-1-propionic acid, described by Bailey and Acree.[2] It showed the characteristic decomposition of the triazole at 240° to a deep-red liquid, and was further identified by a direct comparison with a sample of the triazole, prepared according to the method of Bailey and Acree, by a nitrogen determination, and by being converted into the ethyl ester of the triazole acid (melting-point 171° to 173°).[3]

The semicarbazone of the ethyl ester of pyruvic acid,

$$NH_2CONHN = C(CH_3)COOC_2H_5,$$
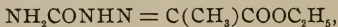
[1] Ber. d. chem. Ges., **33**, 1523.
[2] *Ibid.*, **33**, 1525.
[3] *Ibid.*, **33**, 1527.

does not undergo condensation with sodium alcoholate to form 3,5-dioxy-6-methyl-1,2,4-triazine,[1] as would be anticipated. Repeated experiments were carried out along this line, but in every case the unchanged semicarbazone was regained. The semicarbazone was also heated in the hope of effecting a triazine condensation in this way, but without success. Hydrochloric acid hydrolyzes the semicarbazone. The failure to prepare the triazine from the ester of semicarbazinopyruvic acid is to be regretted, as success in this direction would materially lessen the work in the study of this interesting compound. The semicarbazinopyruvic acid can be obtained almost quantitatively from semicarbazide hydrochloride and pyruvic acid, and the esterification of the semicarbazinopyruvic acid with a yield of over 95 per cent of the theoretical can be effected by boiling with a 3 per cent solution of hydrochloric acid in alcohol.[2]

Semicarbazinoisobutyric Acid,
$NH_2CONHNHC(CH_3)_2COOH$.[3] — For the preparation of this substance semicarbazinobutyramide[4] in 25 times its weight of water is boiled with 0.5 molecule of barium hydroxide until the smell of ammonia disappears. The barium is then precipitated as sulphate, the water evaporated, and the acid crystallized from alcohol. Yield obtained, 55 per cent of the theoretical. The acid, as seen under the microscope, crystallizes in forms resembling cubes. It melts with decomposition at 194°. The acid is readily soluble in water and about 6 parts dissolve in 1,000 parts of alcohol at 25°.

0.1652 gram substance gave 40.6 cc. N at 30° and 746 mm.

0.2651 gram substance gave 0.3628 gram CO_2 and 0.1645 gram H_2O.

	Calculated for $C_5H_{11}O_3N_3$.	Found.
C	37.27	32.32
H	6.83	6.89
N	26.09	26.20

[1] Ann. Chem. (Liebig), **303**, 87.
[2] This esterification was worked out conjointly with C. P. Norby.
[3] The investigation of the butyric acid derivatives and the dimethyltriazine was carried out conjointly with M. B. Wesson.
[4] Ann. Chem. (Liebig), **283**, 36.

The Methyl Ester of Semicarbazinoisobutyric Acid,
$NH_2CONHNHC(CH_3)_2COOCH_3$.—The acid is allowed to
stand nine days with 25 times its weight of a 3 per cent solution
of hydrochloric acid in methyl alcohol, and the ester then
obtained in the usual way. Yield, 80 per cent of the theoretical.
It is readily soluble in cold chloroform, alcohol, and
water, and in hot benzene, and difficultly soluble in ether and
petroleum ether. The ester crystallizes in bunches of long,
slender, microscopic prisms, which melt at 106°.5, apparently
undecomposed.

0.1514 gram substance gave 33.8 cc. N at 27° and 749 mm.
0.2063 gram substance gave 0.3110 gram CO_2 and 0.1385
gram H_2O.

	Calculated for $C_6H_{13}O_3N_3$.	Found.
C	41.14	41.11
H	7.43	7.46
N	24.00	24.28

The Ethyl Ester of Semicarbazinoisobutyric Acid.—This ester
was prepared similarly to the methyl ester and is about as
soluble. It crystallizes from benzene in long, microscopic
prisms, which melt at 97° to a clear liquid.

0.1517 gram substance gave 31.1 cc. N at 27° and 750 mm.

	Calculated for $C_7H_{15}O_3N_3$.	Found.
N	22.22	22.32

3,5-Dioxy-6-dimethyl-1,6-dihydro-1,2,4-triazine,
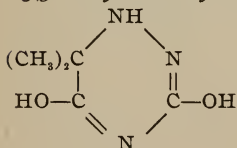
.—This triazine was prepared in the
usual way from the ester and sodium alcoholate. The sodium
salt of the triazine did not separate out of the alcoholic solution.
The triazine is readily soluble in water, more difficultly
soluble in alcohol, and crystallizes from the latter in thin
plates with a silky luster. It melts at 230° to a clear liquid.

0.1741 gram substance gave 0.2683 gram CO_2 and 0.1007 gram H_2O.

		Calculated for $C_5H_9O_2N_3$.	Found.
C		41.96	42.03
H		6.29	6.43

XXXV. — THE ELECTROAFFINITY THEORY OF ABEGG AND BODLÄNDER.

By James Locke.

In reply to the recent article[1] in which Abegg and Bodländer have answered my criticism of their theory of electroaffinity as a basis for the systematization of inorganic compounds, I have little to say beyond adherence to the statements in my first article on the subject.[2] There are a few points, however, involving the question of careless interpretation or rendering of their theory on my part, which I should like to touch upon with brevity before allowing the subject to drop.

The main argument presented in my paper was that the three generic properties, sparing solubility, complex anion formation, and complex cation formation, or the reverse, ready solubility and the non-formation of complex ions, are not necessarily found correlated in the compounds of a given element. We sometimes see among the metallic salts a general sparing solubility without the formation of either complex anions or cations (Tl, Ba, etc.), sometimes difficult solubility and double salt formation without complex cations (Pb, Al, Fe^{III}, Au^{III}, Pt^{IV}, etc.), and sometimes the formation of both complex cations and anions, together with marked general solubility (Mg, Zn, Cd, Co, etc.). It seemed to me that this was a vital objection to their views, and that the assumption that such correlation does exist was not only embodied in their theory, but absolutely necessary to it if electro-

[1] This JOURNAL, **28**, 220.
[2] *Ibid.*, **27**, 105.

affinity were to attain the dignity of a principle by which to classify all inorganic compounds.

My interpretation of their theory in this manner rested upon the fact that in their original paper[1] they devote several pages each to the following propositions :

1. That the solubility of the compounds of a given ion increases with the electroaffinity of the second ion until the electroaffinity becomes very great, in which latter case the effect is to decrease the solubility once more.

2. That the weaker the ions of a salt are (the less their respective electroaffinities), the greater becomes its tendency to form the '' neutral constituent'' of double salts.

3. That the lower the electroaffinity of an ion is, the more will the latter seek to strengthen itself by the addition of such a neutral constituent.

The neutral constituent may be either an ionizing compound, an element (oxygen, sulphur, etc.), or a non-electrolyte, such as ammonia or water. I have reread their first article very carefully, and find no indication of belief on the authors' part that the last two of these three properties are not directly commensurate with the electroaffinity. In the absence of a direct or indirect statement to the contrary, thereupon, it might naturally be taken for granted that these two properties are correlated with one another, and also with the degree of solubility (until '' reverse solubility'' results), since all three vary in the same direction with increasing electroaffinity. Abegg and Bodländer state in their present article, however, that in this respect I totally misunderstand their theory, and that the three properties need necessarily go together only when electroaffinity is responsible for the sparing solubility. They at the same time go to some length to explain that other influences come largely into play. In their first article such other influences were touched upon only once. The attempt was apparently made to trace the properties of all inorganic salts to the electroaffinities of their ions, and only in a single short paragraph, when they were forced to deal with the solubilities of such obstinate bodies as barium

[1] Ztschr. anorg. Chem., **20**, 452.

sulphate, potassium platinichloride, and a few other salts, were outside causes for the behavior of these compounds even hinted at. If at the time of writing that article the authors did not consider the three properties as correlated, how can the following sentence from it (p. 457) be explained?

'' But in these cases (instances in which the decomposition-voltage cannot be measured : L.), as will be shown below, the electroaffinity can be at least approximately estimated from the solubility and the tendency to form complex ions.''

In case no correlation is assumed, why can either property alone be used as a criterion of the electroaffinity? On page 477 we find the solubility used to judge the electroaffinity of oxygen, and solubility and the formation of complex ions for that of sulphur. On page 493 the existence of only simple ions serves as an indication of the high electroaffinity of ammonium. Throughout the entire work one sees, by implication, that sometimes one property is made use of, again another ; how arbitrarily may be shown by an attempt to derive the relative electroaffinities of lead, ferrous iron, and zinc from the degree to which they show the reactions involved. Lead salts are the least soluble, zinc salts form the most stable ammonia addition-products, and iron the most stable double salts. I doubt whether any system based upon such methods can ever become even an approximately useful means of classification. As is apparently recognized by Abegg and Bodländer in their second article, though not at all in their first, their basis of classification is completely hidden through the working of causes unknown, in all except the extreme members of the elements in their system. This being so, their proposition becomes one of adopting for all the elements offhand a system which is obviously applicable only to sodium, silver, and two or three other elements.

In this second paper, Abegg and Bodländer develop afresh their idea of reverse solubility—the decrease in solubility due to the presence in a salt of ions which have exceptionally high electroaffinities. Their remarks in this connection are so worded as to indicate that I had overlooked this point in their theory. I spoke of it as something without which the theory

in general could not stand for an instant. In their original article they state that owing to this reverse solubility effect "the salts of potassium, which has a higher electroaffinity than sodium, are in general less soluble than those of the latter." Here we have a concrete, hard and fast application of their theory to very soluble salts, emphasizing relatively very slight differences in solubility. They now state that "a single general law in the case of easily soluble compounds is not to be expected"—a direct tergiversation. That no such law can be applied in this particular case, and, therefore, that their original view of the relative solubilities of potassium and sodium salts is meaningless, is shown at once if we consider the compounds of more than two metals of high electroaffinity. Starting with zinc, the reverse solubility effect apparently becomes very great as we pass successively through the salts of calcium, strontium, and barium. Then, through lithium, it falls again until sodium is reached. In potassium it becomes stronger once more, only to sink away very noticeably in rubidium and, finally, caesium, which has the highest electroaffinity of all the metals. Caesium chloride dissolves in, at most, one-half its weight of water. I doubt whether, exclusive of the platinichloride, there is a single simple caesium salt which is less soluble than the corresponding potassium compounds. In my own experience with the metal, and this has been quite extensive, I have never found such a case. There is then, absolutely no regularity in the working of the reverse solubility effect, and the relative solubility of potassium and sodium compounds must be referred to some of the unknown causes which Abegg and Bodländer now bring forward to explain the numberless exceptions to their theory, instead of being regarded as a very striking confirmation of the latter.

According to statements in their original article, the authors regard basic salts as compounds of the anion X^- with the cation $M^{II}(OH)^+$. I mentioned the fact that, since according to this the metallic ion is "strengthened" by the addition of hydroxyl, a basic chloride should, by the theory, be more soluble than the normal chloride. Recognizing this sequence, they now suggest that the basic salt probably dis-

sociates in the sense $M^{II}X^+$ and $(OH)^-$, and support their view by the fact that basic salts are usually more soluble than the hydroxides. These two conceptions of the nature of a basic salt are far too fundamentally distinct and important to be slurred over lightly, and the passage from the one view to the other so suddenly by Abegg and Bodländer shows how arbitrarily one must proceed in order to make fact fit the theory.

Whether this particular change in view is of benefit may be doubted. Although the decomposition-voltage of hydroxyl is greater than that of chlorine, the authors assumed it, originally, to have a lower electroaffinity, probably to account for the fact that while chlorides are usually soluble, almost all hydroxides are insoluble. This assumption becomes, in fact, so very important that (p. 477) they regard tendency to hydrolysis as one of the best criteria of the electroaffinity of a metallic ion.

Adopting for basic salts the original formula, $M(OH)^+X^-$, this view is in accordance with their statements that when one of two ions enters into a complex it will be the weaker which does so (as in the compounds K^+, HSO_4^-, and H_2^+, $^+HgCl_4^-$, when K^+ and H^+, Hg^{++} and H^+, are the ions in question). But this formula would require that basic salts be more soluble than normal salts. If we choose the other formula, still holding to the view that hydroxyl has a low electroaffinity, then the relative solubility of the hydroxide and basic salt is explained, but the above very pretty differentiation between acid salts and complex acids becomes meaningless. These two points can be reconciled only by the assumption of a high electroaffinity in hydroxyl—and this cannot be admitted because it would require hydroxides to be more soluble than chlorides. Whether the confusion here resulting is hopeless, or can be cleared up by research, remains to be seen. Until it is straightened out, however, electroaffinity can hardly be regarded as a suitable principle by which to systematize the mutual relations of bases, basic salts, normal salts, acid salts, and complex acids. And these occupy by no means inconsiderable space in the field of inorganic chemistry.

Abegg and Bodländer's pedagogical digression, in their last article, on the cause of the decreased solubility of thallous iodide when in the presence of an alkali iodide, is beside the mark. Noyes' work, which they rather captiously point out as if I had been ignorant of it, can be found cited in my article. They entirely pass over the real significance of such reactions of thallous thallium, of which I stated this to be a single example, and that is, that in spite of its low electroaffinity and the sparing solubility of its compounds the element has in the univalent state almost absolutely no tendency to enter into double salts. In their first article the low solubility here is directly ascribed to the low electroaffinity. In their second, as quoted above, they state that only when low solubility is directly due to low electroaffinity need the former be correlated with the formation of complex ions. The behavior of thallium, therefore, assumes some importance as an absolute exception even to the modified views which they now hold.

If a final confirmation is needed of my contention that in electroaffinity, Abegg and Bodländer are proposing, as a general principle of classification, a property which has been developed on, and can be applied to, only the most extreme members of the family of elements, it may be found in their last remark about the solubility of iodates and periodates. I had pointed out that if the ions of the latter are iodine strengthened by the addition of oxygen, then, by the theory, the salts should be more soluble than iodides. Abegg and Bodländer assume that I think the reader will have only the relations of the alkali salts in mind, and pointing out that here the phenomena are due to reverse solubility, they call attention to the fact that with metals which form typically insoluble iodides, the iodates and periodates are the more soluble of the three. I grant freely that this is so. On the one hand, we have sodium and potassium ; on the other, silver, mercury, thallium, and possibly, but not probably, lead. But the alkaline earth metals, the earth metals, all the rare earth metals, iron and its trivalent analogues, magnesium, nickel, and their bivalent analogues, all the metals, in fact with electroaffinities between these extremes, in all their cathionic

forms, are they to be shut out from a general scheme of inorganic classification? The several periodates of all are obtained usually by precipitation. The iodates are almost all either insoluble or at least sparingly soluble. The iodides of all are probably even more soluble than the chlorides.

Here only two assumptions are possible. Either the authors have neglected to examine the literature, even after the contradictory behavior of the iodates and periodates had been pointed out to them, or they now wish to emphasize only the relation of electroaffinity to the properties of compounds of elements for which the latter is extremely high or low. This second assumption must, of course, be adopted. If it is true, then the authors' attitude is entirely different from that taken in their first article. There we find the properties of all the elements ascribed to their electroaffinity. Cupric amines, for instance, are more stable than cuprous, because the electroaffinity of the cupric ions is the less. The alkaline earth metals form no complex ions because of their high electroaffinity. Perchlorates, pyrosulphates, dichromates, are for the same reason more soluble than chlorides, sulphates, chromates; acid phosphates and acid carbonates than the normal salts. On page 474 we find a whole group treated at once. "Descending still further (from the alkali metals, alkaline earth metals, aluminium, and chromium, successively) in the series of decomposition-voltages, and therefore of electroaffinities, one comes to the heavy metals..... The complex compounds of iron, antimony, arsenic, copper, gold, and platinum, are prototypes of such bodies." Here there is certainly no attempt to limit the influence which electroaffinity is supposed to exert.

I hope to have shown in the above that since the publication of their first article, Abegg and Bodländer have very materially changed their attitude in regard to the general applicability of electroaffinity, at present at least, as a means of general classification. It is unfortunate that their answer to my criticism is so worded that this might not be understood by the more casual reader. Electroaffinity, as a property which stands in interesting and apparently very close relation

to the generic features of many salts, is a very different matter from "Electroaffinity : a new principle of chemical systematization." It ceases to be the latter, and becomes the former, as soon as the fact is recognized that in the great majority of cases its influence is almost entirely concealed by that of other, as yet, unknown causes. What the future of the theory may be must remain doubtful. But where its authors have attempted to analyze disturbing causes, in this last paper, as in discussing the irregularities in the formation of ammonia addition-products, one can hardly call their efforts successful. The only causes isolated as yet are such as, according to their first paper, should themselves act with an intensity dependent directly upon the electroaffinity, and which, therefore, should produce no irregularity whatever, but rather bring about still sharper gradation.

BOSTON, MASS., Sept. 15, 1902.

REVIEWS.

INDICATORS AND TEST-PAPERS : THEIR SOURCE, PREPARATION, APPLICATION, AND TESTS FOR SENSITIVENESS. By ALFRED I. COHN, PH.G. Second edition, revised and enlarged. New York : John Wiley & Sons. 1902. Price, $2.00.

The reception which the first edition of this book was accorded has led to the preparation of a second edition in which the recent developments in the line of indicators have been incorporated. It is a very valuable reference book for all who have to deal with the use of indicators or test-papers, and should be readily accessible to every chemist.   J. E. G.

AMERICAN

Chemical Journal

A STUDY OF SOME OF THE SALTS FORMED BY CASEIN AND PARACASEIN WITH ACIDS: THEIR RELATIONS TO AMERICAN CHEDDAR CHEESE.

By Lucius L. Van Slyke and Edwin B. Hart.

The chemical changes taking place during the early stages of the manufacture of cheese have hitherto been little investigated or understood. This is particularly true of the kind of cheese most extensively made in the United States and Canada, commonly called American cheddar cheese. One of the first recognized changes occurring in the process of cheese-making is that produced by the action of rennet upon milk-casein, resulting in the formation of an insoluble curd. The action of rennet, according to Hammarsten's[1] explanation, splits milk-casein into two different compounds, one, the insoluble curd, called paracasein, formed in large proportions ; the other, soluble, albumose-like, called whey proteid, found in small proportions. While Hammarsten's view is still held by many, there is growing evidence[2] that the albumose-like

[1] Maly: Jahrb. d. Thierchemie, **2**, 118 (1872) ; **4**, 135 (1874).
[2] Fuld : Beiträge zur chem. Physiol., **2**, 169 (1902).

proteid found in whey is not a result of the action of rennet, but that it can be produced by actual proteolytic digestion of casein, due to enzymes either present in the milk itself or introduced with the rennet (as pepsin or Glaessner's pseudo-pepsin). Whatever we may ultimately find the exact nature of the action of rennet on milk-casein to be, it is not the only factor at work during and after the formation of the insoluble curd, for there is present at least one other active process during the early stage of cheese-making that has much to do with the production of a " good curd," judged from the practical standpoint of a cheese-maker.

In cheddar cheese-making, one of the first operations is to "ripen" the milk, previous to adding rennet. This is accomplished by allowing the milk to stand for some time at a temperature of about 30° C., or the operation may be hastened by adding to the milk special cultures of acid-producing organisms. This process, commonly known as the " ripening of milk," has for some time been recognized as an acid-producing form of fermentation ; that is, a fermentation caused by the action of lactic-acid organisms on the milk-sugar, resulting in the formation of lactic acid. In ripening milk, the cheese-maker increases the quantity of acid in the milk, not only before adding acid, but continuously throughout the rest of the process of manufacture.

The amount of acid in cheese-curd is roughly measured in a mechanical way by means of the so-called " hot-iron test." When a piece of curd is pressed against a hot iron and then drawn away carefully, fine, silky threads are formed, adhering to the iron. This phenomenon is closely associated with the formation of acid in the cheese-vat, and the length of the strings shown by the hot-iron test is utilized as a crude measure of the amount of acid present and as an indication of when to perform certain operations. Thus, when the curd strings on a hot iron to the length of one-eighth of an inch, the whey is removed from the curd, after which the curd is "packed" in a pile and allowed to lie until it has passed through the so-called " matting" or " breaking-down" pro-

cess, when it furnishes strings an inch or more in length by the hot-iron test. When this stage is reached, the remaining steps of the manufacturing process are at once completed, such as milling, salting, and putting the curd in molds for pressing.

While it has generally been supposed that the presence of some acid, presumably lactic acid, in the cheese-making process is, in some way or other, responsible for the most important changes taking place, such as the shrinking of the curd, the acquired ability to form strings on a hot iron, and the changes in the appearance and plasticity of the curd, no one has ever been able to show in what way these changes were brought about by acids. It has been commonly supposed that the observed changes were purely physical in character and were not the result of chemical changes in the curd. In the following pages it is our purpose to consider more fully than has been previously done the real function of acids in relation to the important changes taking place in cheese-curd during the cheddar process of cheese-making.

Since Sjöquist's[1] investigation, we have learned that proteids can form salts with acids and bases, and this subject has been considerably developed in the last few years. Bugarszky and Liebermann[2] have shown that egg albumin forms with hydrochloric acid a salt analogous to ammonium chloride, which they call albuminum chloride. Osborn[3] has also shown that edestin, the globulin of hempseed, is capable of combining with acids in several different proportions, forming salts having different properties. Panormoff[4] also has recently described definite compounds formed by egg albumin with different acids. So far as we are able to learn, no similar work with milk-casein or with paracasein (milk-casein coagulated by rennet and constituting a large proportion of cheese-curd) has been done. The nearest any one has come to touching this specific line of work was in the case of Danilewsky,[5] who,

[1] Skandin : Arch. für Physiol., **5**, 277 (1894).
[2] Pflüger's Archiv., **72**, 51 (1898).
[3] Ann. Rep. of Conn. Agr. Expt. Sta., **23**, 402 (1900).
[4] Jour. d. Russ. Phys. Chem. Ges., **31**, 556.
[5] Ztschr. physiol. Chem., **7**, 433 (1883).

in the preparation of what he called pure casein, by the use of hydrochloric acid, actually obtained a mixture of the salts of this proteid, one of which is soluble in boiling 50 per cent alcohol, while the other is insoluble. From this behavior he concluded that milk-casein consists of two proteids. Reference will be again made to this.

It may be stated in this connection that in 1882 Weidmann[1] dissolved from Emmenthaler cheese, by hot alcohol, a substance which he called caseoglutin. This substance has been mentioned in the literature a few times since and has been regarded as a peptone-like body, but no one has ever investigated it and nothing has been known of its real nature. We believe that we have found a satisfactory explanation showing its character, which we will give later in this paper.

In our early work relating to the study of the chemical changes taking place in cheese during the process of ripening or curing, we mixed the cheese thoroughly with sand by grinding in a mortar, and completely extracted this with water at 55° C. The residue, insoluble in water, was then treated with a 10 per cent solution of sodium chloride at 40° C. for the purpose of removing any heterocaseose formed during the ripening process. Chittenden[2] had shown that, in a peptic digestion of casein, heterocaseose was formed only in small amounts. When, by our extraction of fresh or partly ripened cheese with dilute salt solution, we obtained amounts of proteid representing often as high as 40 per cent of the total nitrogen present in the cheese, it became apparent that we were dealing with some compound other than heterocaseose.

<center>EXPERIMENTAL PART.</center>

Occurrence of the Salt-soluble Product in Cheese Made in the Presence of Chloroform with and without Acid.

(*1*) *Without Acid.*—Cheeses were made from milk which had been previously heated to 98° C. for the purpose of de-

[1] Landwirtsch. Jahrb., 1882, p. 587.
[2] Studies in Physiol. Chem., Yale Univ., **2**, 156 (1885-6).

stroying all enzymes and bacterial forms present in the milk.
After cooling the milk to the temperature employed in cheese-
making, chloroform was added to the milk to the extent of 4
per cent by volume, in order to prevent any bacterial activity.
As the ability of milk-casein to coagulate with rennet is im-
paired by heat, this property was restored, in one case, by the
addition of a small amount of calcium chloride, and, in the
other case, by passing a stream of carbon dioxide through the
milk for half an hour. The cheeses, made from the milk thus
treated, were left in press over night and were then examined
at once for the salt-soluble product. The determination was
made as follows : Twenty-five grams of the fresh cheese were
ground with sand and extracted with several portions of dis-
tilled water at 55° C., until the extract amounted to 500 cc.
The residue was then similarly extracted with a 5 per cent so-
lution of sodium chloride. The amount of nitrogen in 50 cc. of
this salt extract was determined by the Kjeldahl process.
Table I. gives the results obtained. The figures in paren-
theses indicate the serial numbers of the different cheeses.

(*2*) *With Acid.*—Other cheeses were made exactly like the
preceding, except that lactic acid was added to the milk to the
extent of 0.2 per cent, by weight, of the milk. An examina-
tion of these cheeses, made at once after they were taken from
the press, gave the results stated in Table I.

*Table I.—Amount of Nitrogen in Salt-soluble Extract, Obtained
from Cheeses Made with and without Lactic Acid.*

	Nitrogen, expressed as percent-age of total nitrogen in cheese.		Nitrogen, expressed as per-centage of cheese.	
	Made with ad-dition of cal-cium chloride.	Made with ad-dition of car-bon dioxide.	Made with ad-dition of cal-cium chloride.	Made with ad-dition of car-bon dioxide.
Without acid	2.44 (44)	5.24 (49)	0.76 (44)	0.132 (49)
	2.90 (47)	5.72 (50)	0.76 (47)	0.148 (50)
With acid	27.88 (45)	29.80 (48)	0.87 (45)	0.700 (48)
	26.62 (46)	22.90 (51)	0.84 (46)	0.754 (51)

An examination of this table shows that the amount of ni-
trogen, in the form of the salt-soluble product, was increased

very greatly by the action of the added lactic acid. The cheeses made without acid show small amounts of this salt-soluble product. In the case of Nos. 44 and 47, the salt-soluble product found may possibly be attributed to the slight amount of lactic acid formed in the milk before it was heated, or it may be that neutral paracasein itself is slightly soluble in a dilute solution of salt. There is some basis for this latter supposition, for, in the case of milk taken directly from a cow and immediately etherized and made into curd, these conditions excluding all possible formation of acid, there still appears to be a slight solubility of the neutral paracasein in dilute salt solution.

In the case of Nos. 49 and 50, somewhat more salt-soluble product is found than in 44 and 47. This is undoubtedly due to the effect of the carbon dioxide used, even so weak an acid probably having some limited tendency to form with paracasein a salt-soluble product.

Occurrence of the Salt-soluble Product in Normal Cheese.

In the many normal cheddar cheeses thus far examined by us, this salt-soluble substance is always found. The amounts vary, but the factors causing the variations have not been fully studied yet. For example, the amount of milk-sugar retained in the cheese is one cause of such variations: likewise, any condition affecting the quantitative conversion of milk-sugar into lactic acid. Then again, we have not yet obtained satisfactory control of all the details of the quantitative estimation of this salt-soluble product. Its amount varies also with the age of a cheese. In cheese fresh from press, that is about twenty-four hours old, we have found that from 40 to 78 per cent of the total nitrogen is in the form of the salt-soluble substance, and the amount diminishes more or less as the cheese advances in age, as illustrated by the figures in Table II.

Table II.—*Amount of Salt-soluble Product in Cheeses at Differ-ent Ages.*

Serial number of cheese.	Age of cheese.	Salt-soluble nitrogen, expressed as percentage of total nitrogen in cheese.	Salt-soluble nitrogen, expressed as percentage of cheese.	Water-soluble nitrogen, expressed as percentage of total nitrogen in cheese.	Water-soluble nitrogen, expressed as percentage of cheese.
54	1 day	58.7	2.08	6.78	0.240
"	1 mo.	42.4	1.51	19.30	0.718
"	3 mos.	33.4	1.31	26.02	1.020
31-A	2 weeks	40.7	1.50	15.50	0.569
" B	"	42.8	1.58	16.50	0.608
" C	"	37.4	1.38	16.10	0.584
" D	"	40.8	1.49	15.80	0.589
38-A	3 mos.	16.48	0.58	37.22	1.310
" B	"	17.60	0.63	35.48	1.270
" C	"	19.19	0.71	32.16	1.190
" D	"	21.96	0.83	29.90	1.130
38-A	9 mos.	13.43	0.54	53.24	2.140
" B	"	14.29	0.57	47.75	1.910
" C	"	18.46	0.74	45.64	1.830
" D	"	18.44	0.78	40.91	1.730

An examination of Table II. indicates a general tendency for the amount of nitrogen present in cheese, in the form of the salt-soluble product, to decrease as the cheese advances in age.

An examination of the last two columns of figures in the table shows that, as cheese increases in age, the amount of nitrogen, in the form of water-soluble products, increases. The fact that the water-soluble nitrogen in cheese increases at the same time the salt-soluble nitrogen diminishes, strongly suggests that this progressive proteolysis takes place at the expense of the salt-soluble product. However, we are not in-clined to assert positively that such a relation exists, until we have perfected to our satisfaction the method for estimating the salt-soluble product. In cheese No. 54, one of our latest experimental cheeses, our method of extraction was under better control, and the figures obtained are entirely consistent

with the view that proteolysis in cheese commences with the salt-soluble product. However, the main point to which we wish to call attention in connection with Table II. is that in freshly-made cheddar cheese the salt-soluble product forms a large part of the nitrogen compounds of the cheese.

Nature of the Salt-soluble Product.

(*1*) *A Salt of Paracasein.*—In the case of cheeses made with and without lactic acid, in the presence of chloroform, we have seen that there were large amounts of the salt-soluble product formed when lactic acid was used, and only small amounts when no acid was used. We have also seen that, in the case of normal cheddar cheese, the salt-soluble product occurs in large proportions, increasing in quantity as the milk-sugar disappears, or, in other words, as the amount of lactic acid increases. It, therefore, appeared to us that, in this salt-soluble product, we were dealing with some compound of paracasein and lactic acid, probably a paracasein lactate.

(*2*) *Artificial Preparation of Paracasein Lactate.*—It seemed desirable to attempt the artificial preparation of the salt-soluble product, and to ascertain if it were identical with the substance extracted by a dilute solution of sodium chloride from newly-made cheese. For the purpose of this comparison, the following experiment was undertaken to prepare artificially the salt-soluble product : About 6 liters of skim-milk were coagulated by rennet at 30° C. The resulting curd was well washed with water, drained, and then treated for one-half hour at 50° C. with 3 liters of a 1 per cent solution of lactic acid. By this treatment a turbid solution was obtained, which was filtered from the large residue remaining undissolved, through cloth first and then absorbent cotton. The filtrate, neutralized by dilute potassium hydroxide, gave a copious precipitate which was filtered, washed with water, and redissolved in 1 liter of a 0.5 per cent solution of lactic acid. This solution was filtered and reprecipitated by dilute alkali, and the process of redissolving, filtering, and reprecipitating was repeated twice. The resulting product was finally well washed

with water, suspended in 95 per cent alcohol for 2 days, and, after removal of alcohol by filtration, was extracted twenty-four hours with ether, and dried at 100° C. The substance thus prepared was firm and leathery in texture, greatly resembling in physical properties the product prepared from the salt extracts of cheese. To all appearances, the lactic acid had simply combined with the paracasein, forming a compound soluble in a slight excess of acid, and insoluble in neutral solutions.

(3) *Preparation of Paracasein Lactate Obtained from Cheese.* —Cheese about three months old was extracted with a 5 per cent solution of sodium chloride. To 6.5 liters of this extract lactic acid was added to the extent of 0.2 per cent by volume, producing a flocculent precipitate that rapidly settled. The precipitate was filtered and allowed to drain, in order to remove the large amount of salt adhering. The filtrate gave no further precipitate on addition of more lactic acid. The precipitate was completely soluble in a 0.5 per cent solution of lactic acid, and this acid solution gave an abundant precipitate when neutralized by dilute alkali. This neutralization precipitate was filtered, well washed with water, and then treated, in every respect, as described above in the preparation of the artificial product. In this way 20 grams of each product were obtained.

(4) *Comparison of Natural and Artificial Products.*—The old method of comparing two products by the results of ultimate analysis, in order to establish their likeness or unlikeness, is now recognized as faulty, especially in the case of proteid bodies. Only by cleavage and by quantitative estimation of certain end-products can a reliable basis be found for determining the question of similarity of structure in different compounds.

Determinations of nitrogen, phosphorus, and ash were made in the two products. In addition, 10 grams of each proteid were hydrolyzed by boiling fourteen hours on a sand-bath, under a Liebig condenser, with 60 grams of water and 30 grams of sulphuric acid of sp. gr. 1.84. In the resulting

liquid, ammonia and the hexon bases were determined according to the method of Kossel and Kutscher.[1] The results are given in Table III., together with similar figures obtained by Hart[2] with casein prepared directly from milk by the use of acetic acid without rennet.

Table III.—Comparative Composition of Natural and Artificial Products.

| | Nitrogen, expressed as percentage of total nitrogen, in form of | | | | Percentage of | | |
	Ammo- nia.	Histi- din.	Argi- nin.	Lysin.	Nitro- gen.	Phos- phorus.	Ash.
Natural product	7.65	2.36	7.77	2.21	15.12	0.70	1.51
Artificial "	7.66	2.21	8.08	2.02	15.30	0.91	1.120
Casein	7.34	3.66	9.51	2.31	15.65	0.84	....

The results embodied in Table III. indicate a striking similarity in structure between the salt formed by paracasein with lactic acid, found naturally occurring in cheese, and that artificially prepared, so far as the products of hydrolysis enable us to draw conclusions. This has reference simply to the linking of the nitrogen in the proteid as a whole.

Later, it will be seen that what we had really prepared in both cases was the saturated salt formed by paracasein with lactic acid, and not the unsaturated salt; and, as we shall show, the unsaturated salt is the one soluble in a dilute solution of sodium chloride. The formation of these combinations with acids probably does not involve any deep-seated rupture of the proteid molecule, as can readily be inferred from the results given in Table III. with casein, which furnishes both saturated and unsaturated salts with acids. It is evident that in the preparation of the artificial salt, identical with the proteid extracted from cheese by a dilute solution of common salt, the chief, if not the only, active factor is an acid.

Salts Formed by Combination of Paracasein with Acids.

(*1*) *Salts Formed by Combination of Paracasein with Lactic Acid.*—In the manufacture of cheese, the lactic acid that com-

[1] Ztschr. physiol. Chem., **31**, 165 (1898).
[2] *Ibid.*, **33**, 347 (1900).

bines with paracasein is formed by the fermentation of milk-sugar, the lactic acid combining with the paracasein as rapidly as the acid is formed. It appeared desirable to study the action of lactic acid, used in different amounts, as it is formed in the fermentation process, upon paracasein under well-controlled conditions, and also to compare this action with the one taking place when pure, dilute lactic acid acts upon paracasein directly without any fermentation. For this purpose it was desired to secure paracasein or cheese-curd as free as possible from acid. In order to prevent all acid fermentation, very fresh, sweet milk was treated with ether. In this way it was possible nearly to eliminate the formation of paracasein compounds of lactic acid at the beginning of the experiment, and have as our original working material paracasein as nearly free as possible from salt-soluble compounds. Two analyses of paracasein, thus prepared, showed the presence of 3.90 and 4.34 per cent of the total nitrogen in the form of a salt-soluble compound.

Several bottles were prepared in the following manner : Twenty-five grams of the carefully prepared cheese-curd or paracasein, ground with sand, were placed in each bottle, 50 cc. of water were added, the mixture was thoroughly shaken, and then sterilized. To this common mixture various additions were made in the different bottles, as indicated below :

Series A received 0.5 gram of sterile milk-sugar and a pure culture of lactic acid organism.

Series B received 1.0 gram of sterile milk-sugar and the lactic acid organism.

Series C contained organism and no milk-sugar.

Series D received 0.5 gram of pure lactic acid and no organism.

Series E received 1.0 gram of pure lactic acid and no organism.

Series F received 1.5 grams of pure lactic acid and no organism.

All the bottles were kept at 15°.5 C., and analyses were made at different periods, as indicated in Table IV.:

Table IV.—Influence of Different Amounts of Lactic Acid on Paracasein.

Series.	Grams of milk-sugar used.	Age of mixture when analyzed.	Presence of milk-sugar in mixture, when analyzed.	No. cc. N/10 NaOH required to neutralize 50 cc. of water extract.	Precipitate appeared on neutralizing water extract.	Nitrogen, in form of salt-soluble product, expressed as percentage of total nitrogen.
A	0.5	2 weeks	trace	3.9	yes	30.36
A	0.5	"	none	4.3	"	27.11
B	1.0	"	considerable	5.4	"	23.31
B	1.0	"	"	5.2	"	20.60
C	0	"	none	1.2	no	3.52
C	0	"	"	1.0	"	3.75
A	0.5	1 mo.	"	4.45	yes	40.65
A	0.5	"	"	3.9	"	28.46
B	1.0	"	little	5.2	"	9.76
B	1.0	"	"	4.9	"	7.32
C	0	"	none	0.6	no	3.52
C	0	"	"	0.8	"	4.07
	Lactic acid.					
D	0.5	"	"	3.4	yes	44.72
E	1.0	3 mos.	"	6.4	"	2.17
F	1.5	1 mo.	"	11.4	"	1.62

Attention is called to certain facts shown by the data embodied in the table above.

1. When we used 0.5 gram of milk-sugar, the maximum amount of the product soluble in a dilute solution of sodium chloride was found only after the milk-sugar had completely disappeared, as can be seen by comparing series A at two weeks and one month.

2. When we used 1 gram of milk-sugar the largest amount of salt-soluble product was formed while considerable sugar was still present. As the acid fermentation of the milk-sugar continued, the amount of salt-soluble product rapidly decreased. This is shown by comparing Series B at two weeks and one month.

3. We see the same truth illustrated in Series D, E, and F,

where we added pure lactic acid directly in the different quantities stated. When we added 0.5 gram of lactic acid there was formed a large amount of salt-soluble product, nearly 45 per cent of the total nitrogen appearing in this form. However, when we used 1 and 1.5 grams of pure lactic acid there was practically no salt-soluble product formed.

4. Even in the cases where the largest amounts of lactic acid were used the acid disappeared as free acid. This was shown by making a titration of the water extract of the curd with N/10 sodium hydroxide, using phenolphthalein as indicator. It is readily seen that the number of cubic centimeters of alkali required for neutralization represents a very small amount of acid, compared with that furnished in Series A, B, D, E, and F. The acid had largely combined with paracasein to form products only slightly soluble in water.

The question may be raised here as to what it is in the water extract that neutralizes alkali. In Series C it is, in all probability, direct neutralization by proteid, as no acid was present. In Series F, on the other hand, there is probably some free acid, as an excess of acid was used. In most cases, however, the neutralization is due, apparently, to a water-soluble compound of acid and proteid, as shown by the fact that only in cases where acid was furnished, whether by fermentation or by direct addition, a precipitate appeared on neutralization, and such a precipitate would be expected only in the case of a combination of acid with proteid. The larger the amount of alkali required by the water extract for neutralization, the more abundant was the precipitate appearing on neutralization.

Just here, the main point we desire to consider is an explanation of the fact to which attention has been called above, *viz.*, that from a given amount of paracasein, treated with a certain amount of lactic acid, we obtain a maximum yield of our salt-soluble product, while an increase of acid beyond a given amount decreases the yield of salt-soluble product. Naturally, we might expect that increase of acid would yield an increase of salt-soluble product from a given quantity of

paracasein. How can we explain this? The explanation that agrees most satisfactorily with the experimental data at hand is this: Paracasein combines with lactic acid in at least two different proportions, forming two distinct compounds. One of these compounds is the unsaturated salt and is soluble in dilute solutions of sodium chloride. It is this compound that is present in normal cheddar cheese. The other compound is the saturated salt formed by the combination of paracasein with lactic acid and is insoluble in a dilute solution of salt.

(*2*) *Salts Formed by the Combination of Paracasein with Other Acids.*—Paracasein forms salts also with other acids. Mr. A. J. Patten has determined for us the amounts of acetic, hydrochloric, and sulphuric acids, required to form the unsaturated and saturated salts. In each case acid was added to 25 grams of fresh curd, previously ground with sand, suspended in water, and finally extracted at 55° C. with a 5 per cent solution of sodium chloride.

Table V.—Formation of Compounds by Paracasein and Different Acids.

	Acetic acid.		Hydrochloric acid.			Sulphuric acid.		
Grams of acid used	0.5	1.0	0.15	0.25	0.50	0.15	0.25	0.50
Percentage of total nitrogen found in form of salt-soluble compound	70.0	5.3	27.3	53.0	5.7	19.5	41.5	2.4

In this table the same general results are seen, as in the case of lactic acid. A certain amount of acid forms with a given amount of paracasein a maximum quantity of salt-soluble product, and increase of acid beyond this quantity forms a compound not soluble in a dilute solution of salt.

It also appears from the results given in Table V. that mineral acids are required in smaller amounts than organic acids to saturate paracasein completely.

Salts Formed by Combination of Casein with Acids.

(*1*) *Formation of the Unsaturated Casein Salt.*—We can show that casein readily forms an unsaturated and a saturated salt with an acid. In preparing the unsaturated salt we used 5 cc. of freshly-drawn milk, diluted with 50 cc. of water, warmed the solution to 40° C., and then added N/10 hydrochloric acid until the resulting precipitate settled leaving a clear supernatant liquid, which required 2.7 cc. To this mixture were added 2.5 grams of sodium chloride, thus making a 5 per cent salt solution. On warming, the unsaturated casein chloride completely dissolved. The experiment was repeated several times with a uniform result. On adding more acid to the salt solution the proteid reprecipitated as the saturated chloride of casein. Casein behaved toward acetic acid in the same manner.

(*2*) *Determination of Amount of N/10 Hydrochloric Acid Required to Saturate Casein.*—Fresh milk was drawn from a cow directly into a bottle containing ether, thus checking all acid fermentation. Of this milk 5 cc., containing 0.0261 gram of nitrogen, were diluted with 50 cc. of water that had been boiled free from all carbon dioxide. The mixture was warmed to 40° C. and 10 cc. of N/10 hydrochloric acid were added. It was desired now to determine the amount of hydrochloric acid that had combined with casein. Determinations of the uncombined acid did not give uniform results, when the titration was made directly after the addition of acid. We therefore employed the method of using calcium picrate.[1] There were added 5 cc. of a neutral solution of calcium picrate to precipitate all proteids completely. The precipitate was filtered off and the filtrate treated with N/10 sodium hydroxide, using rosolic acid as indicator. The reactions taking place can be represented, theoretically, as follows :

Casein $(OH)_2$ + 3HCl(excess) = Casein Cl_2 + $2H_2O$ + HCl;
Casein Cl_2 + Ca picrate + HCl =

<div align="right">Casein picrate + $CaCl_2$ + HCl</div>
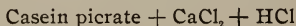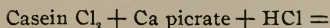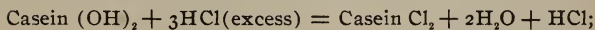
[1] Rohrer: Archiv. für Physiol., **90**, 368 (1902).

When calcium picrate is used, the chlorine which was combined with casein, is changed into calcium chloride, and in this form does not interfere with titration by alkali. Thus we are able to determine more satisfactorily the amount of acid left uncombined with proteid.

In the experiment employed it required 7.4 cc. N/10 sodium hydroxide to neutralize the excess of acid, indicating that 2.6 cc. of acid had entered into combination with 0.0261 gram of proteid nitrogen. Using 6.39 as the nitrogen factor of casein, 0.0261 gram of nitrogen is equivalent to 0.167 gram of casein, and this amount of casein combined with 2.6 cc. N/10 hydrochloric acid, or 1 gram of casein would require for complete saturation 15.6 cc. of N/10 hydrochloric acid. The work was repeated on 5 cc. of milk containing 0.031 gram of nitrogen, and gave 15.9 cc. of N/10 hydrochloric acid as the amount required to saturate 1 gram of casein.

In the manner in which this work was done it is recognized that we were dealing not with casein alone but with the two principal proteids of milk, casein and albumin. However, there is no reason to believe that the results would be essentially different with pure casein. We shall later secure results with casein alone.

(3) *Determination of Amount of N/10 Hydrochloric Acid Required to Saturate the Unsaturated Salt of Paracasein.*—To 50 cc. of the salt extract of some curd, containing 0.058 gram of nitrogen in the form of the unsaturated hydrochloric acid salt of paracasein, were added 10 cc. of N/10 hydrochloric acid for the purpose of converting the unsaturated into the saturated salt. There were then added 5 cc. of neutral calcium picrate to facilitate clear filtration. The mixture was filtered, the precipitate washed, and the filtrate treated with N/10 sodium hydroxide, rosolic acid being used as indicator. Neutralization required 7.1 cc. of N/10 sodium hydroxide. Hence, to saturate the salt-soluble compound, equivalent to 0.058 gram of nitrogen, required 2.9 cc. N/10 hydrochloric acid. Using 6.39 as the nitrogen factor of paracasein, it required 7.83 cc.

of N/10 hydrochloric acid to convert 1 gram of the unsaturated into the saturated hydrochloric acid salt of paracasein.

We saw above that it required from 15.6 to 15.9 cc. of N/10 hydrochloric acid to saturate milk-casein completely, or, more strictly, casein mixed with a small amount of milk-albumin. Now, the amount of N/10 hydrochloric acid required to convert the unsaturated into the saturated hydrochloric acid salt of paracasein, 7.83 cc., is just one-half of 15.7 cc., the amount of N/10 hydrochloric acid required to form a saturated compound. Hence, the amount of combined acid in the saturated salt is twice that in the unsaturated salt; in other words, the unsaturated salt appears to be a mono-acid salt, and the saturated a di-acid salt. These results, it is true, were obtained, in one case, with a milk-casein not strictly pure, and, in the other, with the paracasein derivative of milk-casein; and it may be thought that results secured in this way do not justify the conclusion drawn in regard to the existence of two such distinct combinations of an acid with casein and paracasein. But, aside from the data presented here, we have abundant evidence that both milk-casein and paracasein form at least two salts, corresponding to a half-saturated or mono-acid salt, and a saturated or di-acid salt.

Possibility of an Additional Compound of Paracasein with Acid.

There is evidence that small amounts of acids can disappear in cheese-curd without a corresponding increase of salt-soluble compound. This fact is illustrated by the following experiment: Three liters of freshly-drawn milk, to which ether had been promptly added, were coagulated with rennet and then warmed to 42° C. in order to shrink and harden the curd. Portions of 25 grams each of this curd were ground with sand, placed in Erlenmeyer flasks, covered with 100 cc. of water, heated for ten minutes at 85° C. to check completely all acid fermentation, and then treated with different amounts of lactic acid. After standing one hour, with occasional shaking, the curd in the different flasks was extracted, first with small amounts of water and then with 500 cc. of a 5 per

cent solution of sodium chloride. In 50 cc. of each of these extracts the nitrogen was determined by the Kjeldahl method. The results are given in the following table.

Table VI.—Amounts of Salt-soluble Compound Formed by Different Amounts of Acid.

Grams of lactic acid used	0	0.02	0.05	0.10	0.20	0.50
Percentage of total nitrogen in form of salt-soluble compounds	6.0	7.0	8.1	8.6	23.0	72.0

The amount of salt-soluble compounds was not proportionally increased by the use of 0.02, 0.05, and 0.10 gram of lactic acid for 25 grams of curd, but when an additional 0.10 gram of lactic acid was used, bringing the total up to 0.20 gram of lactic acid, there was a large increase of the salt-soluble compound, and this was still greatly increased by additions of lactic acid above 0.20 gram up to 0.50 gram. It is possible that there may be formed with acids a paracasein salt containing still less acid than the half-saturated salt, or, it may be, that the acid which disappears unites with some of the insoluble inorganic salts in the curd.

Solubility of the Salts Formed by Casein and Paracasein with Acids.

(*1*) *Saturated Salts.*—The saturated acetic and lactic acid salts of casein and paracasein, as well as the hydrochloric and sulphuric acid salts, are practically insoluble in all the media tried. They are insoluble in water, in 5 and 10 per cent solutions of sodium chloride, slightly soluble in 50 per cent boiling alcohol, practically insoluble at 50° C. in saturated solution of calcium carbonate, and in 2 per cent solution of calcium lactate. They dissolve, of course, in excess of acid or dilute alkali.

(*2*) *Unsaturated Salts.*—The unsaturated or half-saturated salt of each of the acids mentioned above is insoluble in water, completely soluble in 5 per cent solution of sodium chloride at 55° or 60° C., not separating again on cooling, but entirely separating by dialysis in water; soluble in 50 per cent boil-

ing alcohol, but separating again on cooling ; only slightly soluble at 50° C. in saturated solution of calcium carbonate, or in 2 per cent solution of calcium lactate.

(*3*) *Explanation of Danilewsky's Error.*—Danilewsky's[1] early supposition that casein consists of two proteid bodies separable by hot 50 per cent alcohol, finds a reasonable explanation in the fact that the unsaturated salt formed by casein with an acid is soluble in 50 per cent hot alcohol, while the saturated salt is insoluble in this medium. When the usual method is employed of precipitating casein from milk by means of dilute acid, the resulting product can easily be a mixture of the unsaturated and saturated salts, the quantity of each present depending upon the amount of acid used in the precipitation. Danilewsky, in his work, used only enough hydrochloric acid to effect a good precipitation of milk-casein, and thus he formed more or less of the unsaturated salt, soluble in 50 per cent hot alcohol. Thus it is easy to see how he came to the erroneous conclusion that milk-casein consists of two proteids.

(*4*) *Weidmann's Caseoglutin.*—Referring again to Weidmann's caseoglutin, dissolved from cheese by hot alcohol, there appears to be every reason to believe that it is identical with the unsaturated paracasein lactate described in this paper.

(*5*) *Relation of Salts to Freudenreich's Results.*—It will be noticed that the solubility of the two salts in a solution of calcium carbonate or calcium lactate is slight. In the case of the saturated paracasein salt, it was found in one experiment that only 1.2 per cent of the salt was soluble at 50° C. in a saturated solution of calcium carbonate, and only 1.12 per cent was soluble in a 2 per cent solution of calcium lactate at 50° C. The unsaturated paracasein salt had a solubility of 5.01 per cent in the solution of calcium carbonate, and 4.70 per cent in the solution of calcium lactate.

The determination of these solubilities was made in the hope of finding some explanation of the results obtained by Freud-

[1] Ztschr. physiol. Chem., **7**, 227 (1883).

enreich[1] in his studies relating to the power of lactic-acid organisms to effect proteolytic changes in milk-casein. Freudenreich found that sterile milk, treated with powdered calcium carbonate and then seeded with certain bacteria that produce lactic acid, showed an increase of soluble nitrogen compounds, in both caseoses and amides. He determined the soluble nitrogen by passing the milk through a Chamberland filter. He does not state the amount of total nitrogen in the milk at the beginning of the experiment, but only the amount of soluble nitrogen. Assuming that the milk used by Freudenreich contained 0.5 per cent of total nitrogen, the average of milk, and recalculating his results in percentages of total nitrogen, we obtain the data given in the following table:

Table VII.—Results of Freudenreich Calculated on Basis of Total Nitrogen in Milk.

Age of milk when analyzed.	Soluble nitrogen, expressed as percentage of total nitrogen in milk.	Amide nitrogen, expressed as percentage of total nitrogen in milk.	Organism used.
Begin'ng of exp't	6.6	....	
9 months	47.0	34.6	Milk culture, Bac. ε from rennet
13 "	44.4	30.2	" " " " " cheese
13 "	49.2	....	" " " " " "
14 "	42.8	28.0	Bac. α and bac. δ
9 "	18.8	10.6	" α

The amounts of soluble nitrogen reported by Freudenreich as being formed by the action of different organisms that produce lactic acid are considerable. Moreover, it is to be noticed that quite large amounts of amide nitrogen were formed. While there were in the flasks used dilute solutions of calcium carbonate and of calcium lactate, we cannot explain the relatively large amounts of soluble nitrogen by the solubility of either the saturated or unsaturated lactates of casein in the solution of calcium carbonate or lactate. Whether his explanation is correct or another is to be found,

[1] Landw. Jahr. d. Schweitz., **12**, 279 (1898).

Freudenreich's results clearly represent actual proteolytic changes of casein.

Nicholson[1] repeated Freudenreich's work, using the common lactic-acid bacterium found in cheese, but failed to find any proteolysis of casein. Nicholson says : '' In some cases, the table shows a slight increase in the soluble nitrogen, where the calcium carbonate has been added ; in others there is no increase. In the uncarbonated milk there is absolutely no increase in any case.'' The slight increase reported by Nicholson in the case of the milk containing calcium carbonate can readily be explained on the basis of the slight solubility of the lactic acid salts of casein in solution of calcium carbonate or calcium lactate.

We have recalculated a portion of Nicholson's results on the same basis as that used with Freudenreich's figures, and give them in the table following :

Table VIII.—Results of Nicholson's Work with Lactic-acid Bacteria.

Without calcium carbonate.			With calcium carbonate.		
Age of milk when analyzed.	Soluble nitrogen, expressed as percentage of total nitrogen in milk.	Amide nitrogen, expressed as percentage of total nitrogen in milk.	Age of milk when analyzed.	Soluble nitrogen, expressed as percentage of total nitrogen in milk.	Amide nitrogen, expressed as percentage of total nitrogen in milk.
0	8.8	3.8	0	9.6	4.0
0	9.2	3.6	0	9.8	4.0
59 days	13.2	3.2	28 days	18.0	4.0
59 ''	12.6	3.0	28 ''	21.8	2.8
450 ''	10.2	1.4	257 ''	12.6	2.2
450 ''	8.4	trace	257 ''	12.2	trace
			314 ''	13.2	2.8
			314 ''	12.0	3.2
			450 ''	12.6	trace
			450 ''	14.0	''

In some of our future work, bearing more directly upon the chemical changes taking place during the process of ripening

[1] Thesis for Master's degree, Univ. of Wis., 1902.

in cheese, we shall have occasion to refer to this subject again.

Relation of the Unsaturated Paracasein Lactate to the Cheddar Process of Cheese-making.

As previously stated, it has been supposed that the presence of lactic acid was, in some way or other, responsible for, or associated with, some of the most important changes taking place in the curd during the cheese-making process, such as the acquired ability to form strings on hot iron and the change in the appearance and plasticity of curd, but no one has previously been able to show beyond question that these changes are actually brought about by an acid, or in what way they are accomplished. We purpose now to show the intimate relation existing between the presence of unsaturated paracasein lactate and some of the important changes occurring in the curd during the process of making cheese.

(*1*) *Property of Curd to String on Hot Iron Due to Unsaturated Paracasein Lactate.*—About 27 liters of milk, properly ripened for cheese-making, were coagulated by rennet, and the process of treatment was carried on in the usual normal manner employed in manufacture. At different intervals samples of curd were taken in order to determine the amount of salt-soluble compound present ; also samples of whey were taken at the same time for the purpose of determining the amount of milk-sugar. The changes took place rather slowly in this instance, owing to the fact that the milk was more than usually sweet for cheese-making purposes, that is, it was so fresh as to contain only small amounts of lactic acid at the start. We present our results below in tabular form :

Table IX.—*Increase of Salt-soluble Compound in Curd with Decrease of Milk-sugar in Whey.*

Time of taking sample of curd.	Percentage of total nitrogen in form of salt-soluble compound.	Percent'ge of milk sugar in whey.	Remarks.
Rennet added at 9.30 o'clock A.M.			
10 o'clock A.M.	5.0	4.75	Curd did not string.
12 " M.	6.1	...	Curd just began to string. Whey removed from curd.
4 " P.M.	31.7	1.83	Curd formed strings 1 inch long. Curd put in press.

The results in this table show that, as the amount of salt-soluble compound present in the curd increased, the curd acquired the property of forming longer strings on the hot iron. That this was due to the increase of salt-soluble compound is confirmed by the fact that the unsaturated salt of casein lactate itself, when isolated from curd or cheese, forms on hot iron beautiful, fine, silky, threads, of almost any length desired. The same is true also of the product artificially prepared.

(2) "*Breaking-down*" *Process in Curd Due to Formation of Unsaturated Paracasein Lactate*.—After the whey is removed from the curd in the process of cheese-making, the curd is "packed" or "matted," that is, piled in a heap and kept in this condition, with occasional repacking, until it has gone through the regular "breaking-down" process, in the course of which the curd undergoes several marked, easily discernible changes in physical properties. From a tough, rubber-like consistency, with a high water-content, the curd changes to a mass of lower water-content, having a smooth, velvety appearance and feeling, and a softer, somewhat plastic consistency. The texture also changes so that the curd acquires a peculiar kind of grain and tears off somewhat like the cooked meat of a chicken's breast.

These marked changes in the physical properties of the curd can be most readily and satisfactorily explained by attributing them to the increasing quantity of the unsaturated casein lactate produced throughout the cheese mass as the result of the continuous formation of lactic acid by the fermentation of the milk-sugar present. These changes in the properties of the curd take place simultaneously with the formation of unsaturated casein lactate and do not take place in the absence of this compound. The softening of curd, or " breaking-down" process, is attributed by Duclaux to the action of *Vibrios*, but this is certainly an error so far as related to American cheddar cheese.

(*3*) *Abnormal Softening of Curd on Addition of Salt, Due to the Presence of the Unsaturated Paracasein Lactate.*—It sometimes happens that, when curd is salted, it softens remarkably, appears to be slimy, and slips through the fingers when squeezed in the hand. This is a condition which has not been satisfactorily explained. The usual explanation is that liquefying organisms have prevailed over all others and have dissolved some of the curd. The real explanation is as follows : When curd behaves, on salting, in the manner described above, more than the usual amount of lactic acid has been formed, and, hence, more than the usual proportion of unsaturated paracasein lactate has resulted. When salt is added to such curd, we at once have a brine formed, which is capable of dissolving the unsaturated paracasein lactate contained in the curd, thus producing a pasty, soft, slippery mass.

In an experiment in which we made cheese from pasteurized milk, we endeavored to simulate the action of lactic acid, as formed by fermentation in ordinary cheese-making, by substituting in its place hydrochloric acid, added in small quantities from time to time, both before and after the addition of rennet. Paracasein chloride was readily formed by the curd, but the use of somewhat too much acid produced an abnormally large proportion of the unsaturated salt, which, on addition of common salt, formed a mushy, slippery mass. The curd, in this condition, was suspended in water and more

hydrochloric acid was added, resulting in the production of a firm, exceedingly hard curd, due to the conversion of unsaturated into saturated paracasein chloride, the latter compound not being soluble in salt solution.

(4) *Amount of Unsaturated Paracasein Lactate in Newly-made Cheese.*—In new cheese, fresh from the press, prepared under normal conditions, we have found as much as 78.5 per cent of the nitrogen compounds present in the form of unsaturated paracasein lactate. The proportion of this compound in new cheese depends upon a variety of conditions which we are engaged in studying. It appears probable that in the case of normal, newly-made cheese the nitrogen compounds consist mainly of unchanged paracasein and unsaturated paracasein lactate, the latter compound being present in larger proportions. Saturated paracasein lactate probably does not occur in normal cheese, but only in cheese made with excessive acid, as, for instance, in the case of cheese made from sour milk.

Relation of Unsaturated Paracasein Lactate to Cheese-ripening.

As cheese ages it undergoes various changes, passing from an indigestible, insoluble, and flavorless substance into the palatable, nutritious material we use as food. The term '' ripening'' is applied to the general process that embraces these changes. Among the most extensive and profound changes occurring in cheese-ripening are those experienced by the nitrogen compounds of the newly-made cheese, chief of which is unsaturated paracasein lactate.

A large amount of bacteriological and chemical work has been done in order to ascertain the cause of the changes that occur in the nitrogen compounds during the ripening of cheese. All of this work has, without exception, assumed that paracasein formed the primary point of attack or the starting-point in these changes. Our results, presented in the foregoing pages, suggest that the unsaturated paracasein lactate, and not paracasein, is the real material with which the process of cheese-ripening commences. It is not our purpose,

at this time, to go into the subject in more than a preliminary way. In connection with Table II., p. 417, attention has been called to the fact that the amount of water-soluble nitrogen in cheese, which is a general measure of the extent of cheese-ripening, increases at the same time the unsaturated paracasein lactate decreases, and probably at the expense of the latter compound.

The belief that the proteolytic changes of cheese-ripening actually start with the unsaturated paracasein lactate, receives confirmatory evidence from the fact that, in the absence of unsaturated paracasein lactate in cheese, we have very incomplete proteolytic change. In order to establish beyond question the specific relation of unsaturated paracasein lactate to the proteolytic changes of cheese-ripening, we have under way numerous experiments in which preparations of pure, unsaturated paracasein lactate are being subjected to the action of a variety of agencies, such as different enzymes and organisms that have been commonly associated with the different theories of cheese-ripening.

Some results already secured appear to indicate that the first proteolytic changes in cheese-ripening are the result of peptic digestion of unsaturated paracasein lactate. In cheese, pepsin appears to act, not to any marked extent upon the proteid paracasein, but only upon its unsaturated compounds with acids. Hence, the function of an acid in cheese-making is the production of the unsaturated compound of paracasein with acid. This suggests that somewhat the same kind of action may be found to be true in the case of gastric digestion. It is well established that pepsin acts upon proteids only in the presence of dilute acid. The function of the hydrochloric acid of gastric juice, like lactic acid in cheese, may be the formation of compounds with proteids; in other words, it may be found that pepsin in gastric digestion does not act upon pure proteids but only upon their compounds with acids, in this case hydrochloric acid. While this general view has been held for some time there have not, so far as we know, been any actual experiments previously made in test-

ing the action of pepsin upon pure compounds formed by proteids with acids. We have done this only in the case of the unsaturated paracasein lactate, but this appears as the first instance to furnish proof in an individual case of what may be found true, in general, of all cases of peptic digestion.

Summary.

1. The object of the work described in this paper is to study the real function of acids in relation to the important changes taking place in cheese curd during the cheddar process of cheese-making.

2. In examining cheese for heterocaseose, by extraction with a dilute solution of common salt, a body was found in quantities so large as to indicate that it was some compound other than heterocaseose.

3. In studying cheeses made with and without the use of lactic acid, the salt-soluble product was discovered to be present in very large quantities only when acid was used, being practically absent, or present in very small proportions, when no acid was used.

4. In normal cheese the salt-soluble product is always found, but in varying quantities, being largest usually in new cheese and diminishing as the cheese ages. Various conditions affect the amount in new cheese, especially those conditions influencing the amount of acid present.

5. Paracasein, carefully prepared and treated with dilute lactic acid, furnishes a product resembling in both physical and chemical properties the salt-soluble substance extracted from cheese.

6. Paracasein is shown to combine with an acid in at least two different proportions, forming two distinct compounds : one is the unsaturated or mono-acid salt ; the other is the saturated or di-acid salt. Such compounds were prepared with lactic, acetic, hydrochloric, and sulphuric acids.

7. Casein forms salts with acids in the same manner as paracasein.

8. The unsaturated salts formed by casein and paracasein with acids are soluble in dilute solutions of sodium chloride and in hot 50 per cent alcohol, but are insoluble in water. The saturated salts are practically insoluble in water, dilute salt solutions, and hot 50 per cent alcohol. Both forms are sparingly soluble in dilute solutions of calcium carbonate and calcium lactate.

9. The important changes taking place in cheese-curd during the process of cheddar cheese-making, such as the acquired ability to form strings on hot iron, the changes in appearance, plasticity, and texture, and probably the shrinking, are due to the formation of the unsaturated paracasein lactate.

10. The ripening process in normal cheddar cheese, by which the insoluble nitrogen compounds change into soluble forms, begins not with paracasein, as has been universally held, but with unsaturated paracasein lactate. The water-soluble nitrogen in cheese generally increases as the unsaturated paracasein lactate decreases, and apparently at the expense of the latter compound. The first step in the normal ripening process of American cheddar cheese is probably a peptic digestion of unsaturated paracasein lactate. Some of the facts presented suggest a method of proof of the commonly accepted theory of gastric digestion.

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ON THE RELATION OF HYDRIODIC ACID AND OF ITS SALTS TO THE STARCH AND DEXTRIN IODIDES.

BY F. E. HALE.

There has been much disputation and uncertainty about the presence of hydriodic acid, or its salts, in starch iodide. Mylius,[1] in 1887, found hydriodic acid and iodine present in starch iodide in the ratio of 1 molecule of hydriodic acid to 4 atoms of iodine, by the treatment of filtrates from starch iodide

[1] Ber. d. chem. Ges., **20**, 688–695.

precipitated in the presence of known amounts of iodine and potassium iodide. Lonnes,[1] in 1894, corroborated Mylius' work by a similar method and found the ratio HI : 4I. Lonnes also analyzed the filtered and washed starch iodide and found a different ratio, HI : 3I, for which fact he offered no explanation, though he mentioned that there always appeared in his wash-water free iodine which he estimated by thiosulphate. As the influence of potassium iodide upon the starch iodide reaction is so marked it seemed proper to investigate again the amount of hydriodic acid, if any, present in starch iodide. After many failures with unsatisfactory methods the following method was devised and carefully carried through with results closer than those of Mylius and Lonnes, and corroborating the ratio HI : 4I for starch iodide.

The starch solution was made from pure potato starch which had been washed with cold water and dried in a vacuum desiccator over sulphuric acid. The consistency of the starch solution was that of a thin paste. As no cellulose settled out and the solution could not be filtered, it was used just as it was. It was made up approximately in 0.5 per cent solution.

The principle of the first and most exact method of analysis consisted in precipitating completely as the starch iodide by an excess of starch solution the free iodine of an exactly measured amount of iodine solution, made up as usual with potassium iodide, and determining the amount of potassium iodide removed from the iodine solution by the starch iodide. The details are as follows :

Into a 500 cc. standard flask 200 cc. of a 0.5 per cent starch solution (the amount determined by experiment) and 10 cc. of dilute sulphuric acid (1 : 3) were introduced, and 40 cc. of N/100 iodine solution were run in from a burette. The mixture was thoroughly shaken, diluted to the mark, shaken again, and allowed to settle. In three to twenty-four hours the starch iodide settled to the bottom of the flask. By means of a suction-pump the supernatant colorless liquid was drawn off into a dry flask, and then was filtered through a dry filter-paper to remove small amounts of starch iodide. Of this

[1] Ztschr. anal. Chem., 1894, p. 409.

liquid, 250 cc. were drawn from a 100 cc. burette into a Drexel wash-bottle (Fig. 1.) fitted with a ground-glass stopper carrying the usual inlet and outlet tubes. To the inlet tube had been sealed a separating-funnel to serve for the introduction of reagents, and to the outlet tube a Will and Varrentrapp bulb-tube charged with a fairly concentrated solution of potassium iodide to catch the iodine carried off mechanically by escaping carbon dioxide during the neutralization of the acid by acid potassium carbonate. Through the separating-funnel 5 cc. of a 0.5 per cent iodic acid solution were added, the proper amount of sulphuric acid being already present in the solution since sulphuric acid had been used to precipitate the starch iodide, and the mixture thoroughly shaken and allowed to stand for five to fifteen minutes. Iodic acid in excess liberates all the iodine of hydriodic acid under proper conditions, as worked out by Gooch and Walker[1] in this laboratory, according to the equation

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$
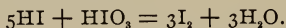
Therefore, five-sixths of the iodine set free represents the hydriodic acid present. The solution was then neutralized, gradually and with thorough shaking, and made alkaline by means of about 50 cc. of a saturated solution of acid potassium carbonate, 50 cc. of $N/100$ arsenite introduced, the contents of the trap added, the trap thoroughly washed, and the excess of arsenite titrated by $N/100$ iodine, with starch as an indicator. The standard of the $N/100$ iodine was determined by the $N/100$ arsenite at 500 cc. volume and in the presence of the same amount of potassium iodide as was introduced into the trap to catch escaping iodine. Five-sixths of the difference between the standard for 50 cc. of $N/100$ arsenite in terms of $N/100$ iodine and the amount of $N/100$ iodine necessary to titrate the excess of arsenite above, represents the amount of iodine corresponding to the amount of potassium iodide left in the iodine solution by the starch iodide. As 40 cc. of

[1] Am. J. Sci., 1897, p. 293.

N/100 iodine were taken, diluted to 500 cc., and 250 cc. of this solution used, the amount of potassium iodide determined was that left in 20 cc. of the N/100 iodine solution. Hence the potassium iodide originally present in 20 cc. of the N/100 iodine solution had to be determined in a similar manner. Into the trapped bottle 20 cc. of the N/100 iodine solution were drawn, 5 cc. of iodic acid and 5 cc. of dilute sulphuric acid (1 : 3) introduced, the mixture shaken after introducing potassium iodide into the trap, and the analysis proceeded with as in the previous case, except that from the total iodine liberated the free iodine of the 20 cc. of N/100 iodine had to be subtracted before finding five-sixths. The difference between the amount of potassium iodide originally present and the amount left there by the starch iodide is the amount used in forming starch iodide.

Analyses.

Standardization.—In the presence of 25 cc. of acid potassium carbonate, 10 cc. of potassium iodide solution, and 3 to 5 cc. of pure starch solution in a total volume of 500 cc., 50 cc. of N/100 arsenite required 50 cc. of N/100 iodine to bring a pale-blue color in two duplicates.

Determination of Potassium Iodide in 20 cc. of N/100 Iodine Solution.

	I. N/100 iodine solution. cc.	II. N/100 iodine solution. cc.
50 cc. N/100 arsenite solution	50.00	50.00
Excess of arsenite solution	5.30	5.20
Free iodine of 20 cc. N/100 iodine and total iodine set free by iodic acid	44.70	44.80
Free iodine of 20 cc. N/100 iodine sol.	20.00	20.00
Iodine set free by iodic acid	24.70	24.80
$\frac{5}{6} \times I$ by iodic acid $= I$ of potassium iodide in 20 cc. N/100 iodine solution	20.58	20.67

Average—20.63 cc. N/100 iodine $=$ iodine of potassium iodide in 20 cc. of N/100 iodine.

Determination of the Ratio of Iodine to Potassium Iodide in Starch Iodide.

	N/100 iodine. cc.
50 cc. N/100 arsenite solution	50.00
Excess of arsenite solution	31.24
Iodine set free by iodic acid	18.76
$\frac{5}{6} \times 18.76 =$ iodine of potassium iodide left in 20 cc. N/100 iodine	15.63
Iodine of potassium iodide in 20 cc. N/100 iodine	20.63
Iodine of potassium iodide left in 20 cc. N/100 iodine	15.63
Iodine of potassium iodide in starch iodide	5.00

But 20.00 cc. N/100 iodine = iodine of starch iodide; therefore, the ratio of potassium iodide to iodine in starch iodide is 1 : 4.

In five other analyses the excess of arsenite was found to be represented by the following amounts of N/100 iodine: 31.20 cc., 31.39 cc., 31.38 cc., 31.14 cc., 31.24 cc., which give the ratio of potassium iodide to iodine as 1 : 4.03, 1 : 3.91, 1 : 3.91, 1 : 4.07, 1 : 4.

These analyses, which point to an average ratio of 1 : 3.99, are so close that they seem to prove absolutely the presence and amount of hydriodic acid in starch iodide.

An attempt was now made to analyze the starch iodide itself. The principle of the method consists in treating the washed starch iodide with an excess of arsenite, titrating the excess by iodine (thus determining the amount of iodine in the starch iodide), determining the total amount of potassium iodide now present and the amounts introduced during the analysis, and so by difference the amount of potassium iodide in the starch iodide. The details are as follows:

The precipitates of the previous experiments were filtered by means of ordinary filter-paper, drained, and washed by filling the funnel four to five times with dilute sulphuric acid (10 cc. of 1 : 3 acid diluted to 500 cc.), and allowing to drain almost or quite dry. A few drops of the final wash-water

gave no test for iodine on adding iodic acid and shaking with chloroform. The precipitates were transferred to beakers by scraping with a glass rod and directing a strong stream of water against them from a wash-bottle, and allowed to settle. The supernatant water was poured off and 50 cc. of N/100 arsenite and 25 cc. of acid potassium carbonate were added to each beaker. In twenty-four hours to a week all the iodine had been taken up. The excess of arsenite was then titrated and gave, by difference, the amount of iodine. The beakers were nearly filled with alcohol (total volume about 400 cc.), and thoroughly stirred to precipitate the starch, as it was found that iodic acid did not free all the iodine from the hydriodic acid in the presence of so much starch. The starch was filtered on asbestos in a Gooch crucible, and quantitatively determined in one case. Before filtering it was absolutely necessary to let the starch settle, and during filtration to keep water out of contact with the starch, else the starch became pasty and clogged the filter. Washing with absolute alcohol every little while was necessary to keep the filter open. The starch was finally washed with ether and a Bunsen flame fanned beneath the crucible until the odor of ether was imperceptible. The crucible was allowed to stand in a sulphuric acid desiccator and weighed. It was then ignited until all starch was burned out, and weighed again. The difference gave the amount of starch. The filtrates were evaporated to dryness on the steam-bath to get rid of the alcohol and ether, the residue taken up with a little water, washed into the Drexel wash-bottle, and the total potassium iodide determined as before, except for the amounts of reagents used. This amount of potassium iodide represents three distinct amounts, the potassium iodide of the starch iodide, the potassium iodide formed from the free iodine of the starch iodide and of the iodine solution introduced, and the potassium iodide always present in the iodine solution introduced. The amount of potassium iodide in 20 cc. of N/100 iodine was determined in the previous experiments and so could be calculated for any amount. The amount of potassium iodide formed from free iodine is converted back into free iodine and

is represented by the iodine value for 50 cc. of N/100 arsenite. The amount of potassium iodide in the starch iodide is found by subtracting the two latter amounts from the total.

Analyses.

	I. N/100 iodine. cc.	II. N/100 iodine. cc.
50 cc. N/100 arsenite	50.00	50.00
Excess of arsenite solution	30.00	24.70
Iodine of starch iodide	20.00	25.30
110 cc. and 105 cc. N/100 arsenite	110.00	105.00
Excess of arsenite solution	5.68	4.60
Total iodine set free by iodic acid	104.32	100.40
$\frac{5}{6} \times$ 104.32 and 100.40 = iodine of potassium iodide freed by iodic acid	86.93	83.67
50 cc. N/100 arsenite	50.00	50.00
Iodine of potassium iodide in iodine solution introduced and in starch iodide	36.93	33.67
Iodine of potassium iodide in iodine solution introduced	31.46	25.58
Iodine of potassium iodide in starch iodide	5.47	8.09

Ratio of potassium iodide to iodine $\left\{ \begin{array}{ll} 5.47 : 20 & 8.09 : 25.30 \\ 1 : 3.66 & 1 : 3.13 \end{array} \right.$

Another analysis of a smaller amount, made by a similar method, but without precipitating the starch, gave a result of 1.67 : 5.12. The ratio is 1 : 3.07.

While the amount of potassium iodide in these analyses is somewhat increased, yet the results are so irregular that they seem to be only roughly corroborative of the ratio obtained by the more exact method. It is more than probable that this increased ratio is due to the difficulty of washing out the last traces of included potassium iodide from the starch iodide.

The Red Starch Iodide.—The influence of concentrated potassium iodide upon the color of starch iodide has been noted by many writers. Mylius,[1] in 1895, noted the power of

[1] Ber. d. chem. Ges., **28**, 385.

water to destroy the red color produced by iodine and concentrated potassium iodide, and suggested that the red starch iodide contained no potassium iodide, but twice as much iodine as the blue starch iodide, performing, however, no experiments to prove his idea. On account of the fact that concentrated potassium iodide turns starch iodide blue to starch iodide red, that potassium iodide is so soluble in water and water turns the red to blue again, it seems more probable that the amount of potassium iodide is increased in the red starch iodide and dissolved out again by the water to reform the blue; that is, it requires considerable concentration of the potassium iodide solution to keep the requisite amount of potassium iodide in the starch red. As Mylius gives the grouping (I.) to starch blue, so I would suggest the grouping (II.) for starch red ; the former grouping answers to the ratio 1 : 4, the latter 1 : 2.

$$H-I \begin{cases} I \\ I \\ I \\ I \end{cases} \qquad\qquad H-I \begin{cases} I= \\ I= \end{cases}$$
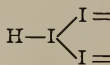
I. II.

It may be, too, that the amount of iodine also changes.

It is a very difficult problem to isolate the starch red, but the following experiments tend to corroborate the above theory :

If starch iodide blue is washed with a concentrated solution of potassium iodide the blue changes to red. This action is hastened and the color deepened by washing with 95 per cent alcohol, or better with absolute alcohol. The alcohol seems to help by removing water, for dilute alcohol restores the blue color as well as water. As a preliminary experiment, about 0.25 gram of starch in 1 per cent solution was treated with 1 cc. of N/10 iodine, and the resulting starch iodide precipitated by dilute sulphuric acid, washed with water, and then washed with a concentrated solution of potassium iodide and with absolute alcohol. It was washed ten to twenty times with the alcohol, but even then free iodine and potassium iodide continued to appear in the alcohol. This red

precipitate was washed into a beaker, arsenite added, and the
analysis made as with the starch iodide blue, the starch being
precipitated by alcohol.

	I. N/100 iodine. cc.
50 cc. N/100 arsenite	50.00
Excess of arsenite solution	43.60
Iodine of starch red	6.40
125 cc. N/100 arsenite	125.00
Excess of arsenite	7.80
Total iodine freed by iodic acid	117.20
$\frac{5}{6}$ × 117.20 = iodine of potassium iodide freed by iodic acid	97.67
50 cc. N/100 arsenite	50.00
Iodine of potassium iodide in iodine solu- tion introduced and in starch red	47.67
Iodine of potassium iodide in iodine solu- tion introduced	45.08
Iodine of potassium iodide in starch red	2.59

The ratio of potassium iodide to iodine is 2.59 : 6.40 =
1 : 2.47.

The presence of free iodine in the alcohol washings appears
to be explained by the supposition that the alcohol washed it
out from the starch iodide blue or red in the presence of the in-
creased amount of potassium iodide. This view is supported
by the fact that in the analysis almost half of the iodine orig-
inally present in the starch blue had been washed out, being
reduced from about 10 cc. of N/100 iodine to 6.4 cc.

Three more analyses were now made with larger quanti-
ties. Into 100 cc. of a 0.5 per cent solution of starch 20 cc.
of N/100 iodine were run and the starch blue precipitated by
sulphuric acid and filtered. The precipitate was washed with
concentrated potassium iodide and with 95 per cent alcohol.
The washing with alcohol was continued until the precipitate
began to turn purplish and the analysis carried out as before.

	cc. N/100 iodine.		
	II.	III.	IV.
50 cc. N/100 arsenite	50.00	50.00	50.00
Excess of arsenite solution	32.35	31.73	37.05
Iodine of starch red	17.65	18.27	12.95
115 cc. N/100 arsenite	115.00	115.00	115.00
Excess of arsenite	5.95	6.38	1.40
Total iodine freed by iodic acid	109.05	108.62	113.60
$\frac{5}{6} \times$ 109.05, 108.62, and 113.60 = iodine of potassium iodide freed by iodic acid	90.88	90.52	94.67
50 cc. N/100 arsenite	50.00	50.00	50.00
Iodine of potassium iodide in iodine solution introduced and in starch red	40.88	40.52	44.67
Iodine of potassium iodide in iodine solution introduced.	33.37	32.73	38.22
Iodine of potassium iodide in starch iodide red	7.51	7.79	6.45

Ratio of potassium iodide to iodine $\left\{ \begin{array}{l} 7.51 : \ 7.79 : \ 6.45 : \\ 17.65 \ \ 18.27 \ \ 12.95 \\ 1 : 2.35 \ \ 1 : 2.35 \ \ 1 : 2.01 \end{array} \right.$

When the difficulties of the analysis are considered, including the fact that the starch red had to be washed until it had commenced to change back to the blue compound so as to be sure that no potassium iodide was held mechanically, the results of the analyses may be taken as corroborative of the theory. My theory of the structure of the starch iodide red as compared with the starch blue is, then, that in the presence of a sufficiently concentrated solution of potassium iodide, helped also by the absence of water, the group $(KI.I_1)$ changes to two groups of $(KI.I_2)$, and that the addition of water removes 1 molecule of potassium iodide, reducing the two latter groups to the former, thus explaining the change of color to red or blue according as potassium iodide is introduced in excess or washed out with water.

In a previous article[1] it has been shown that amidulin is intermediate between starch and dextrin. This fact is also

[1] Am. J. Sci., 1902, p. 379.

shown by the relation of amidulin to potassium iodide, for amidulin iodide blue is far more susceptible to its influence than is starch iodide, that is, solutions of potassium iodide of much less concentration give a reddish tinge to amidulin blue. Concentrated potassium iodide gives to erythrodextrin red an orange-brown tone, not so yellowish, but more reddish, and far deeper than the color of iodine in potassium iodide in blank.

Some further interesting results come out of these analyses. Of the 0.5 per cent starch paste employed it took 200 cc. to completely precipitate 40 cc of $N/100$ iodine solution. If 50 cc. of $N/100$ iodine were added a distinct yellow color was visible in the filtrate, or supernatant liquid. The one analysis mentioned showed that all the starch came down with the starch iodide. Mylius[1] found a ratio of iodine to starch iodide which answered to the formula $[(C_6H_{10}O_5)_4I]_4.HI$. Rouvier[2] found a ratio in his starch iodide leading to $(C_6H_{10}O_5)_8I$. He precipitated with an excess of starch and thought that the excess of starch explained the difference, as Mylius precipitated with iodine in excess. In my experiments the starch was in excess, and taking the fact into account that 1 gram of the starch paste used was a bare excess for 40 cc. of $N/100$ iodine, the starch iodide answers to $[(C_6H_{10}O_5)_{16}I]_4.HI$, that is, my starch paste, which was rather viscous, appears to have been twice as large a molecular body as Rouvier's starch and four times as large as Mylius' starch.

Wholly apart from the consideration of theory, the influence of iodides upon the delicacy of the starch blue test for iodine is sometimes a matter of considerable practical importance analytically. In standardizing certain thiosulphate solutions by iodine in presence of acid, Norris and Fay,[3] finding that they obtained a higher standard at the temperature of ice-water than at the ordinary laboratory temperature, have attributed that fact to the greater delicacy of the starch blue reaction at low temperatures. It is evident that these investigators have mistaken the occasion of variation in their

[1] Ber. d. chem. Ges., **20**, 688.
[2] Compt. rend., **114**, 1366–1367.
[3] This JOURNAL, **23**, 125.

standards in overlooking the well-known influence of potassium iodide, always present in standard iodine solutions, upon the starch iodide reaction. Under the actual conditions of standardizing, the use of even 10 cc of N/10 iodine as ordinarily made up in potassium iodide implies the simultaneous introduction of, or production of, over 0.3 gram of potassium iodide. Experience shows that the presence of this amount of potassium iodide in so much as 300 cc. of total dilution is sufficient to make the readings by the starch indicator quite as delicate at ordinary temperatures as at the temperature of ice-water, and the addition of an excess of potassium iodide above this amount does not render the reading any sharper. The following table demonstrates the exact agreement of the readings under the two sets of conditions, the presence of sufficient potassium iodide at ordinary temperature, and the presence of 10 cc. of hydrochloric acid at the temperature of ice-water :

Table I.

Volume. cc.	Potassium iodide. (0.1–0.3 gram.)	Hydrochloric acid. (Sp. gr. 1.12.) cc.	Temperature.	Pure potato starch solution. cc.	Sulphuric acid. cc.	N/10 iodine. cc.	Thiosulphate. cc.
300	....	10	6^{o1}	2	.	25	35.26^2
"	....	10	6°	2	.	25	"
"	1 crystal	..	23°	2	5	25	"
325	1 "	..	23°	2	5	25	"

The sharpness of the readings in the two first titrations is not due solely to the low temperature or to the presence of the hydrochloric acid, but mainly to the potassium iodide introduced and formed, which fact is clearly shown in the following table, which gives the results obtained when a N/1000 solution of iodine was used under varying conditions :

[1] The temperature was taken at the end of the titration.
[2] The thiosulphate was run in 0.1–0.2 cc. at a time until near the end, and then by drops.

Table II.

Volume. cc.	Potassium iodide not exceeding 0.3 gram. cc.	Hydrochloric acid (Sp. gr. 1.12). cc.	Pure potato starch solution. cc.	Temperature.	N/1000 iodine. cc.	Color.
100	1 crystal	..	2	A 23°	0.45	Faint-blue
200	"	..	2	23°	0.65	"
300	"	..	2	23°	0.80	"
400	"	..	2	23°	1.30	"
300	"	..	2	B 23°	0.80	"
300	"	..	2	5°.01	0.70	"
300	....	..	2	C 23°	9.20	"
300	....	..	2	5°.01	1.50	"
300	....	1	2	D 23°	4.15	"
300	....	10	2	23°	4.00	"

In the absence of a sufficient amount of potassium iodide (C) the influence of temperature is very noticeable, but in the presence of potassium iodide (B), though not exceeding 0.3 gram, and at a dilution of 300 cc., no closer reading could be obtained at the temperature of ice-water than at the ordinary laboratory temperature. In the absence of potassium iodide, even at the temperature of ice-water, the reading was almost twice as large as that obtained in the presence of potassium iodide at the ordinary temperature. An increase in the amount of hydrochloric acid did not materially increase the sharpness of reading (D), and the reading was fully five times as large as that obtained by the influence of potassium iodide. The first four experiments (A) show that the total volume has considerable proportionate influence upon the amount of iodine needed for a reading. These experiments are in agreement with Lonnes'[2] work.

[1] At the temperature of ice-water the blue color had a greenish tinge.

[2] Ztschr. anal. Chem., 1894, p. 409.

ON THE DIBROMDINITROBENZOLS DERIVED FROM PARADIBROMBENZOL.

[SECOND PAPER.[1]]

BY C. LORING JACKSON AND D. F. CALHANE.

The mixture of isomeric dibromdinitrobenzols obtained by the action of nitric acid and sulphuric acid on paradibrombenzol was first studied by Austen,[2] who isolated two of the isomers, which he distinguished by the prefixes α and β. Later he established the constitution[3] of the β-substance as

$$Br_2 1,4, (NO_2)_2 2,6.$$
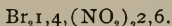
The structure of Austen's α-isomer has been determined recently by one of us and Wheeler[4] as $Br_2 1,4, (NO_2)_2 2,3$.

In his first paper on this subject Austen mentioned a body melting near 120°, which he took to be the third isomer, but in the last of his papers in the *Berichte* he announced his conclusion that this substance was a mixture and not a new isomeric form. In continuing the work we have succeeded in obtaining this third isomer, and, as it melts at 127°, it is not improbable that it formed part, at least, of the body observed by Austen. We obtained it from the mother-liquors left after the α-isomer had crystallized from the solution of the crude product in glacial acetic acid. For this purpose the solid matter was precipitated with water, and, after being dried, extracted with ice-cold ether, in which the new γ-isomer was practically insoluble, whereas the β-modification went into solution. The yield was less than 10 per cent of the crude material, the yield of the α-isomer somewhat over 5 per cent, and although it is obvious that considerable amounts of these isomers remained in the mother-liquors, so that these yields are far from representing the quantities formed, yet there is no doubt that the β-isomer is the principal product of the reaction.

[1] First paper, Calhane and Wheeler: This JOURNAL, **22**, 451.

[2] Ber. d. chem. Ges., 8, 1183; **9**, 621, 918.

[3] Am. J. Sci., [3], **16**, 46.

[4] Calhane and Wheeler : *Loc. cit.*

There are only three dinitro compounds which can be derived from paradibrombenzol,

a-159°. β-99°-100°.
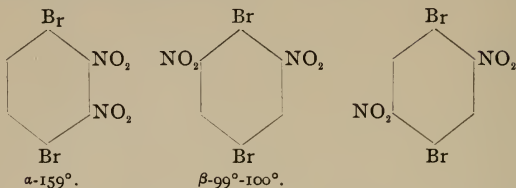
and, as the constitution of the α- and of the β-isomers has been determined, it follows that the new isomer must have the structure $Br_2 1,4, (NO_2)_2 2,5$. We thought it worth while, however, to test this inference by experiment, and accordingly reduced the new dibromdinitrobenzol to a diamine with tin and hydrochloric acid, and then oxidized this diamine with a mixture of sulphuric acid and potassic dichromate, when we obtained the dibromquinone $C_6H_2O_2Br_2$, melting at 187° to 188°, made by Sarauw[1] from dibromhydroquinone by oxidation. As our sample of the quinone was made from paradibrombenzol, its constitution must be $Br_2 1,4, O_2 2,5$, and the constitution ascribed to our isomer, $Br_2 1,4, (NO_2)_2 2,5$, is confirmed. We may add that the diamine gave, with ferric chloride and sulphuretted hydrogen in acid solution, the blue color characteristic of paradiamines.

The 1,4-dibrom-2,5-dinitrobenzol melts at 127°, so that its melting-point lies between those of the vicinal (α) form, 159°, and the unsymmetrical (β) form, 99°–100°. It is a decidedly reactive substance, and we have studied some of its derivatives, but the large outlay of time necessary to prepare it in quantity has prevented us from carrying this work so far as we could have wished.

The 1,4-dibrom-2,5-phenylenediamine obtained by reducing the dinitro compound with tin and hydrochloric acid (zinc dust and acetic acid give a less pure product) melts at 183° to 184° and forms a chloride, $C_6H_2Br_2(NH_3Cl)_2$.

Alcoholic ammonia at 100° gives with the γ-dibromdinitro-

[1] Ann. Chem. (Liebig), **209**, 112.

benzol the 1,4-dibrom-2-nitro 5-aminobenzol (2,5-dibrom-4-nitraniline) $C_6H_2Br_2NO_2NH_2$, melting at 174° to 175°, by the replacement of one nitro by an amino group, but the yield is very small. Ammonic bromide is also formed in the reaction, which points to another organic product. This, however, we did not succeed in isolating from the viscous residues.

Aniline gives the 1-brom-4-anilido-2,5-dinitrobenzol,

$$C_6H_2BrC_6H_5NH(NO_2)_2,$$
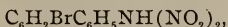
an orange-red compound melting at 153° to 154°. We did not succeed in finding a second modification of this substance, although we looked carefully for it, because the occurrence of two modifications of such nitranilido compounds has been observed[1] several times in this laboratory.[2]

Sodic ethylate in the cold replaces one of the nitro groups by an ethoxy group forming the dibromnitrophenetol,

$$C_6H_2Br_2NO_2OC_2H_5, (OC_2H_5)1, Br_2 2, 5, (NO_2)4,$$

which melts at 126°. It is curious that this substance melts only 1° below the dibromdinitrobenzol from which it was formed, and resembles it so closely in crystalline form and solubility that the only indication of a reaction was the formation of sodic nitrite. The reaction runs quickly and neatly. No sodic bromide could be detected among the products. If the sodic ethylate acted at the boiling-point of alcohol, a bromine atom was also replaced by an ethoxy group, giving a bromnitrodiethoxybenzol, $C_6H_2BrNO_2(OC_2H_5)_2$, melting at 103° to 104°. This compound may be either a resorcin ether, $(C_2H_5O)_21,3,Br_4,NO_26$, or a pyrocatechin ether, $(C_2H_5O)_21,2, Br_4,NO_25$. An attempt to determine its constitution with an insufficient amount of substance seemed to show that it was a pyrocatechin ether, because an alcoholic solution of the free phenol gave a precipitate with an aqueous solution of plumbic acetate. We do not, however, attach much weight to this

[1] Jackson and Beutley : This JOURNAL, **14,** 348 ; Jackson and Herman : *Ibid.*, **16,** 35 ; Jackson and Cohoe : *Ibid.*, **26,** 5.

[2] The observation, that bromine was replaced when aniline acted with the γ-isomer, whereas the nitro group was replaced when ammonia was used, has no real significance, because probably with both reagents parallel actions affecting the bromine and the nitro group took place, but in each case we failed to isolate more than one of the products.

experiment, as, when performed on so small a scale, it was impossible to guard with certainty against the numerous sources of error. On the other hand, the atom of bromine replaced to form a pyrocatechin ether is in the meta position to the nitro group, whereas the atom of bromine replaced, if a resorcin ether was formed, is ortho to the nitro group ; as all previous experience in such replacements has shown that the loosening effect of a nitro group in the meta position is much slighter than that of one in the ortho position, we think it much more probable that the substance is a resorcin ether than a pyrocatechin derivative in spite of the experimental evidence ; accordingly we have assigned this constitution to it provisionally.

An experiment was tried on a small scale with a boiling solution of sodic hydrate and the dibromdinitrobenzol, which showed that both sodic nitrite and bromide were formed, and that, therefore, the reaction runs in essentially the same way as that with hot sodic ethylate. Lack of material prevented us from studying the organic products, which promised to be of only slight interest. For the same reason the product of the action of sodic malonic ester on the dibromdinitrobenzol was not studied, although a preliminary experiment showed that a red salt was formed.

We have also studied the behavior of the α-1,4-dibrom-2,3-dinitrobenzol with sodic ethylate in the cold. The reaction ran much less rapidly and neatly than that with the 2,5-dinitro compound, sodic nitrite was formed with little more than a trace of sodic bromide, and the product consisted principally of unmanageable tars. We succeeded, however, in isolating a dibromnitrophenetol, $C_6H_2Br_2NO_2.OC_2H_5$, formed by the replacement of one nitro group by an ethoxy group, which must have the constitution $Br1,4,NO_22,(OC_2H_5)3$. It melts at $45°$ and the yield was 18 per cent. In spite of many experiments we are unable to give any account of the other products of the reaction. If the reaction between the 1,4-dibrom-2,3-dinitrobenzol and sodic ethylate was carried on at the boiling-point of alcohol, nearly 15 per cent of the total amount of bromine was converted into sodic bromide, so that

this reaction is undoubtedly similar to the one observed with the γ-compound under the same conditions. With alcoholic ammonia at 100° about 13 per cent of the bromine in the α-body was converted into ammonic bromide. This result corrects the statement of Austen[1] that no ammonic bromide was formed under these conditions.

The 2,3-dinitro compound, when boiled with an aqueous solution of sodic hydrate, gave, by the replacement of one nitro group by hydroxyl, the 2,5-dibrom-6-nitrophenol, which melts at 77° and forms the yellow, slightly soluble barium salt, $(C_6H_2BrNO_2O)_2Ba.3H_2O$. Only a very small amount of sodic bromide was formed in this process.

In their behavior with reagents the two isomers,

$$Br_2 1,4,(NO_2)_2 2,3 \quad \text{and} \quad Br_2 1,4,(NO_2)_2 2,5,$$
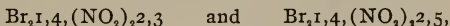
show a strong similarity. In both cases a nitro group is more easily replaced than the bromine, as shown by the action of a cold solution of sodic ethylate, but one of the atoms of bromine can be replaced without much difficulty. It was observed repeatedly, however, that the 2,5-dinitro body was much more sluggish in its action than the 2,5-dinitro compound. The only difference in the structures of these isomers is that in the first the nitro group which is replaced by another radical, is in the ortho, in the second in the para position to the other nitro group, and these observations, therefore, are in harmony with the quantitative results of C. A. Lobry de Bruyn and Alph. Steger,[2] who found that the speed of substitution of a nitro group by the ethoxyl radical is nine times as great in paradinitrobenzol as in orthodinitrobenzol.

In our work with both these dibromdinitrobenzols we observed no sign of the replacement of bromine by hydrogen in reactions with sodic ethylate, the search for which had led us to undertake the study of these compounds. Tin and hydrochloric acid also failed to remove the bromine from the γ-2,5-dinitro compound, but this is not surprising, as we can

[1] Ber. d. chem. Ges., 9, 622.
[2] Rec. trav. chim. Pays-Bas, 18, 9; Steger : *Ibid.*, 13.

find[1] no case of such a removal of bromine from paradinitro compounds.

γ-Isomer.

Isolation of 1,4-Dibrom-2,5-dinitrobenzol.—The crude product from which this substance was extracted was made by the action of fuming nitric acid and strong sulphuric acid upon paradibrombenzol, as follows :[2]   Two hundred grams of para-dibrombenzol (made by the method of Jannasch[3]) were dissolved in 650 grams of fuming nitric acid of sp. gr. 1.505, and mixed with the same volume of strong sulphuric acid, which caused the precipitation of a red oil.   Disregarding this, the mixture was warmed, and as soon as a violent action set in the source of heat was removed until it had come to an end. The liquid was then boiled gently, for three hours, in a flask closed with a porcelain crucible, after which it was allowed to cool, and, before the oil had solidified, poured into a large quantity of water contained in an evaporating dish for convenience in removing the solid, which formed after standing over night.   The crude product amounted to 246 grams.

This product of the reaction, after washing with water, was dissolved in glacial acetic acid (85 cc. of acid to each 50 grams of the substance), and allowed to stand in a cold place, when a quantity of the α-isomer $(Br_21,4,(NO_2)2,3)$ crystallized out. The mother-liquor from this, when precipitated with water, furnished a mixture of all three isomers, which was treated as follows :   Fifty grams of this mixture were digested with 175 cc. of ether for one hour, the mixture being cooled with snow or ice during this time, and stirred continually, taking care to break up the lumps as much as possible to aid the solvent action of the ether.   The undissolved portion was filtered out, and in this way 38 grams, insoluble in ether, were obtained from 300 grams of the crude material.   The ethereal solution was evaporated and the residue put aside to be worked up for

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[1] This JOURNAL, 18, 465.

[2] Austen : Ber. d. chem. Ges., 9, 621 ; Calhane and Wheeler : This JOURNAL, 22, 451.

[3] Ber. d. chem. Ges., 10, 1355.

the β-isomer in the future. The 38 grams of impure dibrom-dinitrobenzol, insoluble in ether, melted at 105°. They were divided into two lots of 19 grams, and each of these recrystallized from 250 cc. of alcohol, which gave 22 grams of nearly pure product from the 38 grams of crude substance. One more crystallization from alcohol raised the melting-point to 127°, where it remained constant. It was dried at 100° and analyzed with the following result :

I. 0.2503 gram substance gave, by the method of Carius, 0.2892 gram of argentic bromide.

II. 0.2656 gram substance gave 22.2 cc. N at 31° and 761 mm.

	Calculated for $C_6H_2Br_2(NO_2)_2$.	I.	II.
		Found.	
Br	49.08	49.16	....
N	8.59	....	9.03

The substance is, therefore, the third dibromdinitrobenzol derived from paradibrombenzol, and has the constitution $Br_2 1,4, (NO_2)_2 2,5$, as proved later in this paper.

Properties of the 1,4-Dibrom-2,5-dinitrobenzol.—When crystallized from a mixture of benzol and alcohol it forms. at first short prisms with two edges truncated by a basal plane and terminated by two planes. As the crystals grow, one of the terminal planes becomes· developed at the expense of the other, so that the final form consists of long, rather slender, prisms, terminated by a single plane at an oblique angle. The crystals apparently belong to the monoclinic system, and show a tendency to twin by uniting along the edges. It was also observed in arborescent forms having a general resemblance to those of ammonic chloride. It is white with a pale-yellowish tinge, and melts at 127°. It is soluble in benzol, chloroform, acetone, or carbonic disulphide; slightly soluble in ether; slightly soluble in cold, soluble in hot alcohol; slightly soluble in cold, readily soluble in hot amyl alcohol, or glacial acetic acid; practically insoluble in cold, sparingly soluble in hot ligroin; practically insoluble in water. Strong hydrochloric acid or strong sulphuric acid has no apparent action, hot or cold. Fuming nitric acid does not seem to af-

fect it when cold, but dissolves it when hot. The action of sodic hydrate upon it is described later in this paper. The best solvent for it is alcohol.

Reduction of the *1,4-Dibrom-2,5-dinitrobenzol.*

The reduction was made both with tin and hydrochloric acid, and with zinc dust and acetic acid. The first method is to be preferred, as it gives a white, pure product at once, whereas the product from the action of zinc and acetic acid is usually highly colored, and can be purified only with difficulty.

Three grams of the dibromdinitrobenzol were mixed in a flask with 150 cc. of strong hydrochloric acid and about 30 cc. of alcohol. An excess of granulated tin and a piece of platinum foil were then added and the mixture heated on the steam-bath under a return condenser until all the organic matter had gone into solution, which usually occurred in eight hours. At the beginning of the process the crystals took on a deeper yellow color, and later a white, flaky body was precipitated, which afterward went into solution. After the reduction had come to an end the clear solution was poured off from the excess of tin and, on cooling, began to deposit white, feathery crystals of a double salt of tin, which were dissolved by the addition of more water, and then sodic hydrate was added until the liquid showed a strong alkaline reaction. The quantity of sodic hydrate used was not enough to redissolve all the hydrates of tin, as this would have given an inconveniently large volume of liquid. The alkaline liquid with the suspended hydrate of tin was next extracted with ether, the ether extract shaken with aqueous sodic hydrate, which dissolved out the hydrate of tin taken up by the ether, and the clear ethereal solution allowed to evaporate. The residue was a white, waxy substance, which turned brown on exposure to the air. As it still contained a quantity of inorganic matter it was treated with hot benzol and filtered ; the deep-yellow filtrate, on cooling, deposited pearly plates, which showed the melting-point 183° to 184°, and as repeated crystallization from benzol did not raise this melting-point, the substance was obtained pure without recrystallization.

The reduction with zinc and acetic acid was carried on as follows: Three grams of the 1,4-dibrom-2,5-dinitrobenzol mixed with 60 cc. of glacial acetic acid somewhat diluted with water were warmed gently on the steam-bath, and to the mixture zinc dust was added from time to time until 9 grams had been used and the heating had continued for four hours. During this time the color of the solution changed from yellow to deep-purple. Upon the addition of a large quantity of water to the product a black precipitate was formed, which weighed about 2 grams, and, therefore, contained the larger part of the reduction-product. The filtrate had a dark-purple color, but yielded very little organic matter, when extracted with ether direct, or when the ether extraction was preceded by treatment with sodic hydrate. The black precipitate was dissolved in boiling benzol and filtered hot. The filtrate, which had a deep mahogany-brown color, deposited long, brown needles as it cooled, which retained their color even after several crystallizations from benzol with the aid of bone-black. This strong and persistent color, and the fact that the substance crystallized in needles instead of the plates observed with the diamine prepared by tin and hydrochloric acid, made us suspect at first that this substance was not the diamine, but on determining its melting-point we found it to be 181° to 182°, and this was so near that of the diamine (183°) that it seemed more probable that it was really the diamine and that the color and difference in crystalline appearance were due to the presence of a clinging impurity. This latter view was proved to be correct by substituting chloroform for benzol in the purification of the product, when, even at the first crystallization, the color was removed in great measure, and it crystallized in plates instead of needles. A second crystallization from chloroform gave white plates melting at 183°, identical with those prepared by tin and hydrochloric acid. In describing the preparation of the diamine by zinc and acetic acid we mentioned that the product was treated with hot benzol to dissolve the brown diamine; there was left after this treatment a bluish-purple mass insoluble in benzol, which was amorphous and bulky. We are inclined to

think that this consisted principally of the diamine protected from solution in the benzol by a still larger amount of the impurity contained in the brown needles, since this bluish-purple substance also melted at about 183°. It may be added that the brown crystals were decolorized by reduction with tin and hydrochloric acid, yielding the diamine, crystallizing in plates, and melting at 183°.

A sample of the diamine dried at 100° gave the following result on analysis :

0.1395 gram substance gave, by the Carius method, 0.1971 gram argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	60.12

This analysis is confirmed by the analysis of the chloride of the diamine given later.

Properties of the 1,4-Dibrom-2,5-phenylenediamine.—When crystallized from chloroform it appears in large, white plates[1] with a pearly luster, which turn brown on exposure to the light. A freshly prepared and recrystallized sample melted at 183° to 184°. When it melts the substance is converted into a dark-blue body, possibly identical with the impurity which gave so much trouble in purifying the product from zinc and acetic acid. We have not attempted to investigate this compound on account of the difficulty of preparing the diamine on a large scale. The diamine is soluble in ether or acetone ; slightly soluble in alcohol, benzol, chloroform, glacial acetic acid, or ligroin, when cold, more soluble in each of these solvents when hot. Chloroform is the best solvent for it, but in bringing it into solution long or vigorous heating should be avoided, as this causes decomposition. Strong hydrochloric acid has no action on it, when cold. When the mixture is heated, a small amount of the diamine is dissolved, but the action is too incomplete to use this method to advantage in forming salts. Strong nitric acid acts vigorously, forming a yellow body with a marked quinone odor. Fuming nitric acid acts with explosive violence, converting the diamine into a

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[1] As mentioned above, when impure it may crystallize in needles instead of plates.

black tar. Strong sulphuric acid has no effect in the cold, but dissolves the diamine when hot. On cooling, a crystalline body separates, which is perhaps the sulphate. With sodic hydrate there is no apparent action, whether hot or cold. Two experiments with ferric chloride showed that it acted on the diamine dissolved in acetone, but no definite oxidation-products could be isolated with the small amount of material at our disposal. The diamine, when mixed with ferric chloride and sulphuretted hydrogen in dilute acid solution, gave a purple product similar to Lauth's violet.

Chloride of the 1,4-Dibrom-2,5-Phenylenediamine,

$C_6H_2Br_2(NH_3Cl)_2$.—This salt was prepared by saturating with hydrochloric acid gas a solution of the diamine in dry benzol. The white precipitate thus obtained was washed with benzol, dried in a desiccator, and analyzed with the following result:

0.2009 gram substance gave, by the Carius method, 0.3927 gram of the mixture of argentic chloride and argentic bromide.

	Calculated for $C_6H_2Br_2(NH_3Cl)_2$.	Found.
Cl and Br	68.14	68.14

Properties.—The chloride of the diamine, when crystallized from a boiling, moderately dilute solution of hydrochloric acid, forms long, slender, white needles with a vitreous luster. It is not very stable, as a specimen of it turned green in a single night when exposed to the air of the laboratory. Upon heating it seems to be decomposed into hydrochloric acid and the free diamine, which sublimes. It dissolves in boiling water apparently without decomposition, but is only very slightly soluble in boiling strong hydrochloric acid. The best solvent for it is somewhat diluted hydrochloric acid.

Constitution of the Third Isomeric Dibromdinitrobenzol Derived from Paradibrombenzol.

Although the constitution of this isomer was essentially established by exclusion[1] as $Br_2 1,4, (NO_2)_2 2,5$, we thought it necessary to confirm this inference by experiment. Accord-

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[1] See the introduction to this paper.

ingly the diamine, made by the reduction of the dibromdini-
trobenzol with tin and hydrochloric acid, was oxidized as fol-
lows : Eight grams of strong sulphuric acid were diluted
with 32 cc. of water and the mixture cooled to zero by im-
mersing it in ice. One gram of the dibromphenylenediamine
was dissolved in this and then 1 gram of powdered potassic
dichromate was added in small portions at a time with care-
ful stirring. The mixture was allowed to stand over night,
after which it was cooled again to zero, and 1 gram more of
potassic dichromate added with the same precautions as be-
fore. It was now allowed to stand three or four hours and
then extracted with ether. Upon allowing the ether to evap-
orate, yellowish-brown grains were obtained with an unmis-
takable quinone smell, which, after recrystallization from
alcohol, were converted into short, golden-yellow prisms melt-
ing at 187° to 188°. The substance, therefore, is evidently
the dibromquinone, which melts at 188°, obtained by Sarauw[1]
by oxidizing dibromhydroquinone with ferric chloride, and
this inference is confirmed by the agreement in the other
properties of the two bodies, both of which show similar solu-
bilities and sublime in small needles. As Sarauw prepared
this substance from hydroquinone, and we made it from para-
dibrombenzol, it can have only the structure $Br_2 1,4,O_2 2,5$, and
it follows, therefore, that the constitution of our dibromdini-
trobenzol must be $Br_2 1,4,(NO_2)_2 2,5$. This constitution was
also confirmed by the fact that our diamine, when treated
with sulphuretted hydrogen and ferric chloride in acid solu-
tion, gave the deep-blue coloration characteristic of the para-
diamines.

Action of Alcoholic Ammonia on 1,4-Dibrom-2,5-dinitrobenzol.

Our work on this subject is not so complete as we could
wish, since the experiments here described exhausted our
supply of the γ-isomer, and the importance of this part of the
research was not sufficient to justify the large expenditure of
time necessary to provide a new supply.

Half a gram of the dibromdinitrobenzol was sealed in a tube
with 15 to 20 cc. of a saturated solution of ammonia in abso-

[1] Ann. Chem. (Liebig), **209**, 112.

lute alcohol and heated to 100° for five or six hours. At the end of this time the tube was opened and its contents, after driving off the alcohol, washed thoroughly with water. The wash-water gave a strong test for a bromide with argentic nitrate and nitric acid. Upon extracting the washed residue with ligroin a substance melting between 135° and 139° was obtained, but in too small amount for investigation. The portion insoluble in ligroin was next treated with benzol containing a little alcohol, and in this way another compound was extracted, which, after recrystallization, melted constantly at 174° to 175°. It was dried at 100° and analyzed with the following result:

0.1480 gram substance gave, by the Carius method, 0.1856 gram argentic bromide.

	Calculated for $C_6H_2Br_2NO_2NH_2$.	Found.
Br	54.05	53.37

The substance was formed, therefore, by the replacement of one nitro by an amino group, and is 1,4-dibrom-2-nitro-5-aminobenzol (2,5-dibrom-4-nitraniline). The yield was very small, so that the principal product was contained in the residue insoluble in benzol, and was probably formed by the reaction which produced the ammonic bromide found in the wash-water.

The 1,4-dibrom-2-nitro-5-aminobenzol crystallizes in deep brownish-yellow prisms, which melt at 174° to 175°. It is sparingly soluble in cold, more soluble in hot benzol. The benzol solution, if treated with hydrochloric acid gas, gives a precipitate of a salt in yellow needles.

Action of Aniline on the 1,4-Dibrom-2,5-dinitrobenzol. Bromanilidodinitrobenzol, $C_6H_2BrC_6H_5NH(NO_2)_2$. *Br1,* $C_6H_5NH4,(NO_2)_2$ 2,5.

In spite of the fact that the dinitro compound dissolved in aniline even in the cold, imparting a deep-red color to the liquid, some preliminary experiments had indicated that the action took place slowly even at 100°. We proceeded, therefore, as follows: The substance was heated on

the steam-bath with an excess of aniline for three or more hours, and the product was allowed to stand over night. The excess of aniline was then removed by washing with acid and water, and on testing the wash-waters it was found that bromide of aniline had been formed. The residue, insoluble in water, was a red powder, which was purified by crystallization from alcohol containing a little benzol, until it showed the constant melting-point 153° to 154°, when it was dried at 100° and analyzed with the following result :

0.2463 gram substance gave, by the Carius method, 0.1365 gram argentic bromide.

	Calculated for $C_6H_2Br(C_6H_5NH)(NO_2)_2$.	Found.
Br	23.66	23.58

Properties of Bromanilidodinitrobenzol,

$Br1,C_6H_5NH4,(NO_2)_22,5$.--It crystallizes from alcohol and benzol in six-sided plates not far removed in shape from regular hexagons, which later develop into prisms belonging to the monoclinic or orthorhombic system. Its color is orange-red, somewhat redder than that of potassic dichromate. We could find no evidence that it existed in more than one modification, although we tried in many ways to convert it into a second form, since Cohoe and one of us[1] have found that the bromanilidodinitrobenzol, $Br1,C_6H_5NH3,(NO_2)_24,6$, occurs in a red and yellow modification. It melts at 153° to 154°. It is soluble in ether, benzol, chloroform, glacial acetic acid, or carbonic disulphide ; sparingly soluble in methyl or ethyl alcohol, whether cold or hot ; very sparingly soluble in ligroin. The best solvent for it is ethyl alcohol containing a little benzol. Strong sulphuric acid dissolves it slowly with a deep-violet color, which changes to brown on heating. Nitric acid in the cold has no perceptible effect on it. When hot it dissolves it slowly, forming a deep-orange solution from which nothing is precipitated by dilution. Fuming nitric acid acts vigorously on it in the cold, forming a brownish-black solution, from which water throws down a yellowish-green precipitate. Sodic hydrate has little or no action on it even in hot solution.

[1] This JOURNAL, **26**, 1.

An attempt to prepare a dianilido body by the action of aniline at higher temperatures (175° to 180°) gave an un-promising-looking product, and, as the substance would be of but little importance, we did not pursue this part of the subject further.

Action of a Cold Solution of Sodic Ethylate on the 1,4-Dibrom-2,5-dinitrobenzol.

Five grams of the dibromdinitrobenzol were dissolved in benzol and mixed with the solution of sodic ethylate prepared by treating 0.7 gram of sodium with absolute alcohol, that is, 2 molecules of sodic ethylate were used for each molecule of the dibromdinitrobenzol. As soon as the ethylate was added a flocculent precipitate was formed, and the solution took on a deep wine-red color, which increased in intensity on standing. To make sure that the reaction was complete the mixture was kept at ordinary temperatures in a corked flask for over thirty-six hours, at the end of which time a brick-red precipitate had collected in the bottom of the flask. This was filtered out and proved to be entirely soluble in water. It gave no test for sodic bromide and contained not more than a trace of organic matter, but with an acidified solution of potassic iodide and starch paste it gave a strong test for a nitrite, and upon adding dilute sulphuric acid a copious evolution of red, nitrous fumes was obtained. It was evident, therefore, that the precipitate was principally sodic nitrite. The alcohol and benzol filtrate from this precipitate of nitrite was allowed to evaporate spontaneously and the brownish-white residue washed with water, after which it was recrystallized from hot alcohol until it showed the constant melting-point 126°. The melting-point was, therefore, almost identical with that of the original substance, 127°, and the solubility in alcohol and its appearance were so similar to those of the dibromdinitrobenzol that the formation of the sodic nitrite was the only indication that a reaction had taken place. It was dried at 100° and analyzed with the following result :

0.3082 gram substance gave 12 cc. N at 20° and 760 mm. pressure.

	Calculated for $C_6H_2Br_2.NO_2.OC_2H_5$.	Found.
N	4.31	4.45

The substance contains bromine. It is evidently formed by the replacement of one of the nitro groups by an ethoxy group. The yield was somewhat over 4 grams from the 5 grams of dibromdinitrobenzol, that is, more than 80 per cent of that required by theory.

Properties of Dibromnitrophenetol, $C_6H_2Br_2.NO_2.OC_2H_5$. $(C_2H_5O)1Br_22,5,NO_24.$—When crystallized from hot alcohol it forms at first groups of radiating white needles, which in time develop into slender prisms with blunt ends. It melts at 126°. It is freely soluble in benzol, toluol, chloroform, acetone, or carbonic disulphide; somewhat less soluble in ether or glacial acetic acid; very slightly soluble in ethyl or methyl alcohol when cold, soluble in them when hot; almost insoluble in cold ligroin or amyl alcohol, soluble in these liquids when hot. The best solvent for it is alcohol. Strong hydrochloric acid has no visible effect on it, even when hot. Strong nitric acid also seems to have no action on it in the cold, but when hot dissolves it slowly with a yellow color. On cooling, crystals are deposited which look like those of the original body. Fuming nitric acid dissolves the substance at once, even in the cold. On diluting this solution, a white precipitate is formed. Strong, cold sulphuric acid turns the substance deep golden-yellow with partial solution. When hot the acid dissolves it slowly. Sodic hydrate has no apparent effect, even when hot. Cold aniline dissolves it easily, but on removing the aniline with dilute hydrochloric acid the residue is white, so that the aniline has probably acted merely as a solvent.

Action of a Hot Solution of Sodic Ethylate on the 1,4-Dibrom-2,5-dinitrobenzol.

In an experiment similar to that described in the preceding section, except that the mixture of sodic ethylate and

dibromdinitrobenzol was heated for two hours after standing in the cold, we obtained in addition to the substituted phenetol melting at 126° another substance melting at 103° to 104°. Accordingly we studied the action of a hot solution of sodic ethylate, as follows: Five grams of the dibromdinitrobenzol dissolved in boiling benzol were treated with a hot solution of sodic ethylate in small successive portions. A precipitate was formed immediately as in the reaction with cold sodic ethylate and the liquid turned dark-yellow. After all the sodic ethylate had been added the mixture was boiled for half an hour under a reverse condenser. At the end of this time the precipitate which had formed was filtered out and the dark-yellow filtrate allowed to evaporate spontaneously. The residue was washed with water and the highly-colored wash-waters tested with argentic nitrate and nitric acid, which showed the presence of a bromide in quantity, and with potassic iodide, starch paste and acetic acid, which showed a large amount of nitrite. The remainder of the aqueous solution was acidified with sulphuric acid and extracted with ether, but the amount of oily organic matter thus obtained was too small for investigation. The residue left after washing the product with water was a semi-liquid mass of a terracotta red color, and with a peculiar odor. It was extracted with hot ligroin until only a small tarry residue was left undissolved. On evaporating the dark-yellow ligroin extract a red oil was obtained, which solidified after standing for a short time. After some trouble a satisfactory method of purification was found, consisting in recrystallization from a dilute alcohol, made up of one part of water and three of alcohol, which brought the substance to the constant melting-point 103° to 104°, when it was dried *in vacuo* and analyzed with the following result:

0.3130 gram substance gave 13 cc. N at 22° and 762 mm. pressure.

	Calculated for $C_6H_2BrNO_2(OC_2H_5)_2$.	Found.
N	4.82	4.72

The substance contains bromine. These results show that

it must be formed from the dibromdinitrobenzol by the replacement of one nitro group and 1 atom of bromine by two ethoxy groups. The reaction probably takes place in two stages, the first consisting in the replacement of the nitro group to form the phenetol melting at 126°, which is then converted by the replacement of one of the bromine atoms into the body melting at 103° to 104°. This substance must be either the bromnitroresorcin ether, $(OC_2H_5)_2 1,3, Br4, NO_2 6$, or the bromnitropyrocatechin ether, $(OC_2H_5)_2 1,2, Br4, NO_2 5$. In an attempt to determine its constitution we saponified the very small amount of it at our disposal with dilute sulphuric acid, and obtained from the alcoholic solution of the phenol, with an aqueous solution of plumbic acetate, a yellow, flocculent precipitate. This would indicate that the substance is a pyrocatechin ether, but considering the chances of error in this experiment, we cannot place much confidence in it when tried on such a small scale, and as the formation of a resorcin ether is much more probable than that of a pyrocatechin ether, judging from all previous experience in such replacements, we have decided to call our substance provisionally the resorcin ether.

Properties of the 4-Brom-6-nitroresorcin Diethyl Ether, $C_6H_2BrNO_2(OC_2H_5)_2$.—Crystallized from dilute alcohol it forms sheaves of pointed needles of a yellowish-white color. It melts at 103° to 104°, and is freely soluble in benzol, chloroform, or acetone ; soluble in ether, glacial acetic acid, or carbonic disulphide ; sparingly soluble in ethyl or amyl alcohol, or ligroin, when cold, soluble in each of these liquids when hot. Dilute alcohol containing one part of water to three of alcohol is the best solvent for it. Strong nitric acid has no apparent effect on the substance when cold, but dissolves it slowly when hot ; on dilution, what seems to be the original substance, is precipitated. Fuming nitric acid dissolves it at once, even in the cold. Strong sulphuric acid dissolves it with a red color, even in the cold. Sodic hydrate apparently does not react with it, even when hot. Aniline dissolves it in the cold, but gives no change of color even on heating.

The action of an aqueous solution of sodic hydrate with the

1,4 dibrom-2,5-dinitrobenzol was tried on a small scale in order to determine which radicals were replaced, and sodic bromide and sodic nitrite were found among the products of the reaction, from which it appears that the hot solution of sodic hydrate acts like the hot solution of sodic ethylate, so far as the places of attack are concerned. We did not have material enough to study the organic products of the reaction which were contained in the deep blackish-red solution formed by boiling the two reagents together for three hours. At the end of that time all the organic substances had dissolved with the exception of a very little brown tar.

Sodic malonic ester also acted upon the 1,4-dibrom-2,5-dinitrobenzol, forming a red sodium salt, but we did not succeed with the small amount of material we could spare for this work in isolating the substituted malonic ester, as the product obstinately refused to solidify. For this experiment the sodic malonic ester should be made from sodium and the ester, since, if it is made with sodic ethylate in the usual way, the product is in great part the dibromnitrophenetol melting at 126°, already described.

α-*Isomer.*

Action of Sodic Ethylate on 1,4-Dibrom-2,3-dinitrobenzol (α-Dibromdinitrobenzol).

Five grams of this dibromdinitrobenzol were dissolved in the smallest possible amount of benzol, and mixed with the sodic ethylate prepared by treating 0.7 gram of sodium with 40 cc. of absolute alcohol, that is 2 molecules of ethylate for each molecule of the dibromdinitrobenzol. The mixture gradually took on a dark-red color, and was allowed to stand over night in a corked flask, as it was found that the reaction ran slowly. The liquid mixed with a precipitate which had been formed, was then poured into a dish, and the solvents allowed to evaporate spontaneously. The product, a red, oily mass, was washed three or four times with small quantities of water. The wash-water gave a strong test for a nitrite, a slight test for a bromide. As the residue

did not solidify on standing even at low temperatures, it was extracted several times with boiling ligroin, which left behind a hard, tarry mass of a brick-red color. The solution in ligroin had a lemon-yellow color, and on evaporation left a red oil, which was distilled with steam, when a yellow oil came over, solidifying in the condenser or the receiving-flask. This was filtered out and the filtrate examined for an additional quantity of the product, but it seemed to contain so little that it was not worth while to work it up. The crystalline solid which had come over with the steam was freed from oil by pressing it between pieces of filter-paper, the papers being extracted with ether, and the extract worked up again for the solid substance. As the substance was very soluble in all the common solvents, and its melting-point lay as low as 45°, some trouble was experienced in finding a solvent, which would give crystals. At last, however, we succeeded in purifying it, as follows: A quantity of ligroin (boiling below 70°) was saturated with the substance at a temperature of 50°, and then cooled by immersion in ice, when the body crystallized out in yellow prisms which were washed with ice-cold ligroin and dried between pieces of filter-paper. In this way the substance was obtained with the constant melting-point, 45°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.2153 gram substance gave, by the Carius method, 0.2500 gram argentic bromide.

II. 0.3066 gram substance gave 12.2 cc. N at 18° and 760 mm. pressure. If the determination of nitrogen in this substance is run with only the usual precautions, results more than 2 per cent too high may be obtained. Similar observations have been made frequently in this laboratory in determinations of nitrogen with substances which contain the ethoxy group, and burn with almost explosive violence. The difficulty was overcome, as in previous cases, by distributing the substance through an unusually long layer of fine cupric oxide, and applying the heat with great caution. In this case the greater part of the nitrogen was given off by the heat of conduction before a single burner had been lighted below the layer of oxide and the substance.

	Calculated for $C_6H_2Br_2.NO_2.OC_2H_5.$	Found. I.	II.
Br	49.23	49.41	....
N	4.31	....	4.59

The substance is, therefore, the 2,5-dibrom-6-nitrophenetol, formed by the replacement of one nitro group by an ethoxy group. Oddly enough, another dibromnitrophenetol has nearly the same melting-point, 46°, but they are not identical, since this was made by Städel[1] from the 4,6-dibrom-2-nitrophenol. The yield was far from good, 0.9 gram of the uncrystallized substance being obtained from 5 grams of the dibromdinitrobenzol, which amounts to 18 per cent of the theoretical.

Properties of the 2,5-Dibrom-6-nitrophenetol, $C_6H_2Br_2.NO_2.$ $OC_2H_5.$—Crystallized from cold ligroin it forms long, thick, transparent prisms of a lemon-yellow color. It melts at 45°. It is very soluble in all the organic solvents, even when cold; slightly soluble in water. It is left as an oil by the evaporation of its solutions at ordinary temperatures. The best solvent for it is ligroin, from which it crystallizes well, when the solution saturated at 50° is cooled with ice. Strong nitric acid turns the substance red in the cold; on warming, it melts to a red oil, but does not dissolve. Fuming nitric acid dissolves it at once even in the cold, and on dilution white crystals of what seems to be a new substance are precipitated. Strong sulphuric acid has no apparent action, when cold, and on heating the substance melts but does not dissolve. Sodic hydrate does not affect it either cold or hot. Aniline dissolves it, but, even after heating the mixture, what seems to be the original body is recovered when the aniline has been removed by means of dilute hydrochloric acid.

As has been stated already, the 2,5-dibrom-6-nitrophenetol is not formed in very large quantity (less than 18 per cent) by the action of sodic ethylate on the dibromdinitrobenzol. The other products of the reaction must be contained in the aqueous wash-waters and in the tarry residue left on extraction with ligroin, and we devoted a great deal of time to attempts to isolate some definite compound from these products,

[1] Ann. Chem. (Liebig), **217**, 57.

but all our experiments led to oily substances which did not solidify on standing, and were obtained in too small quantity for distillation, even although in one case the product came from 20 grams of the dibromdinitrobenzol. As, therefore, we could not be certain of the purity of these substances, we did not waste time in analyzing them.

In order to see whether sodic bromide was formed in addition to sodic nitrite, when 1,4-dibrom-2,3-dinitrobenzol was treated with a boiling instead of a cold solution of sodic ethylate, the following quantitative experiment was tried: Two and a half grams of the dibromdinitrobenzol were boiled for three hours in a flask with a return condenser with a solution of sodic ethylate made from 0.35 gram of sodium. The solvent was allowed to evaporate spontaneously, and the residue, after standing some time, was washed with cold water, which took up a large amount of soluble matter. The washings were acidified with nitric acid, and the rather heavy precipitate filtered out, after which the light-yellow filtrate was precipitated with argentic nitrate. In this way 0.4310 gram of argentic bromide was obtained. This corresponds to 14.95 per cent of all the bromine in the substance, and represents the amount converted into sodic bromide in this process.

A similar quantitative study was made of the action of alcoholic ammonia on the 1,4-dibrom-2,3-dinitrobenzol (α). Two grams of the substance were heated for three hours to 100° in a sealed tube with 20 cc. of alcoholic ammonia, after which the alcohol and excess of ammonia were driven off with a blast of air, and the residue washed with water. Addition of nitric acid to the wash-water produced a precipitate, which was filtered out, and the filtrate was then precipitated with argentic nitrate. In this way 0.3018 gram of argentic bromide was obtained. This corresponds to 13.08 per cent of all the bromine in the substance and represents the amount converted into sodic bromide in this process.

Action of Sodic Hydrate in Solution on the 1,4-Dibrom-2,3-dinitrobenzol (α).

Three grams of the substance were mixed with a solu-

tion of pure sodic hydrate made from 1.2 grams of sodium and 150 cc. of water, and the mixture boiled for seven to eight hours in a flask provided with a return condenser. At the end of this time practically all the solid had disappeared, forming a deep-yellow solution which, after it had cooled, was acidified with sulphuric acid and allowed to stand over night. In order to purify the tarry precipitate with some embedded crystals thus obtained it was distilled with steam, which in the course of a day drove over a considerable amount of a golden-yellow solid. This was filtered out and the filtrate yielded by long extraction with ether nearly an equal amount of the product. The steam distillate melted at 77°, and this melting-point proved to be constant on recrystallization from ligroin. The residue left by the steam in the flask was tarry, and gave only unmanageable substances when treated with solvents. The phenol melting at 77° was dried *in vacuo* and analyzed with the following result :

0.1566 gram of the substance gave, by the Carius method, 0.1996 gram argentic bromide.

	Calculated for $C_6H_2Br_2.NO_2.OH.$	Found.
Br	53.87	54.25

This analysis shows that the body is the 2,5-dibrom-6-nitrophenol formed by the replacement of one nitro by a hydroxyl group, and this inference is confirmed by the analysis of the barium salt given later. The yield was fairly good, as 3 grams gave 1.2 grams of product in one case, 1.35 grams in another, which amounts to about 44 per cent and 49 per cent of the theoretical yield. This replacement of the nitro group is, therefore, probably the principal reaction, and this idea is confirmed by the observation that, whereas much sodic nitrite was formed as a secondary product, the amount of sodic bromide was insignificant. It was also observed that the action of the α-isomer with hot sodic hydrate was much more sluggish than that of the γ-isomer with the same reagent.

Properties of the 2,5-Dibrom-6-nitrophenol, $C_6H_2Br_2.NO_2.OH.$ —It appears in bright golden-yellow needles, which melt at 77°. It is easily soluble in alcohol, methyl alcohol, ether, chloro-

form, acetone, acetic ester, or carbonic disulphide; soluble in benzol; slightly soluble in ligroin, or water. Strong sulphuric acid turned it red, but did not dissolve it even when hot; strong nitric acid had no apparent action in the cold, and when hot it dissolved the substance, but no precipitate was formed on addition of water; hot fuming nitric acid, on the other hand, formed a red solution with it, from which water threw down a precipitate. Aniline turned it red, and, if warmed, gave a red solution from which a red solid was obtained by removing the excess of aniline with hydrochloric acid.

Barium Salt of the 2,5-Dibrom-6-nitrophenol, $(C_6H_2Br_2NO_2.$ $O)_2Ba3H_2O$.—This salt was made by boiling the phenol with water in which pure baric carbonate was suspended. The carbonate was decomposed with effervescence and a deep reddish-yellow solution was formed, which was filtered off, and the insoluble part extracted with hot water until the extracts were colorless. The solution was then evaporated until masses of small, yellow crystals separated, which were collected, air-dried, and afterward dried *in vacuo* over sulphuric acid, and then at 100°. Most of the water passed off *in vacuo*, only 1 milligram being lost at 100° from the salt dried *in vacuo*.

0.2100 gram air-dried salt lost 0.0144 gram when heated to 100°.

	Calculated for $(C_6H_2Br_2.NO_2.O)_2Ba3H_2O.$	Found.
H_2O	6.89	6.86

0.1956 gram salt dried at 100° gave 0.0624 gram $BaSO_4$.[1]

	Calculated for $(C_6H_2Br_2.NO_2.O)_2Ba.$	Found.
Ba	18.84	18.78

The salt, with water of crystallization, forms very small yellow crystals, which turn brown when they lose the water. It is slightly soluble in water.

The action of aniline with the 1,4-dibrom-2,3-dinitrobenzol was tried several times by us, and some of these experiments were on a large scale, when the difficulty of preparing material is considered, but in no case did we succeed in obtaining products which could be brought into a state fit for analysis; we can therefore give no account of this reaction.

[1] It is best to treat the salt with dilute sulphuric acid before treating it with the strong acid.

IV.—ON THE AZOXYBENZALDEHYDES.

By F. J. Alway.

In a previous article[1] I have shown that an unidentified compound obtained by Gattermann[2] is identical with that described by Kirpal as "p-azoxybenzaldehyde" and that, when pure, it melts at 190° (uncorr.), as found by Gattermann, the temperature 194°, given by Kirpal,[3] being the corrected melting-point, although it was not so stated. In the same article it was mentioned that Lucius and Brüning[4] had patented a process for the preparation of p-azoxybenzaldehyde, p-azoxybenzylideneaniline, and homologues of the latter from the corresponding p-nitrobenzylaniline, p-nitrobenzyltoluidine, etc. The melting-point of the aldehyde and that of its anilide, as given by Lucius and Brüning, were 10° and 18°, respectively, lower than those of the compound of Gattermann and its anilide. It was pointed out further that as the compound of Gattermann was stable toward concentrated sulphuric acid at temperatures as high as 100°, the azoxy nature of the compound was not established. Since sending in the above-mentioned paper it has been found that the compounds obtained by the method of Lucius and Brüning are identical with those already described, and that they may very readily be obtained by the interaction of p-nitrobenzyl chloride, aniline or its homologues, alcohol, and caustic alkali under certain conditions. The yield by this method, which is published elsewhere, is 75 to 80 per cent of the theoretical amount, while by the other methods it varies from 10 to 40 per cent of the theoretical. As p-nitrobenzyl chloride may be easily prepared by the nitration of benzyl chloride and is much cheaper, if purchased, than p-nitrobenzaldehyde, the last-described method is preferable for the preparation of p-azoxybenzaldehyde and its derivatives.

The compound melting at 190°, when exposed to the prolonged action of concentrated sulphuric acid at a high tem-

[1] This Journal, **28**, 34.

[2] Ber. d. chem. Ges., **29**, 3037 (1896).

[3] Ibid., **30**, 1597.

[4] D. R. P., **111**, 384.

perature, changes into a compound which has all the ordinary characteristics of the oxyazo compounds. This fact leaves no doubt as to the nature of the compound melting at 190°. It is *p*-azoxybenzaldehyde.

m-Azoxybenzaldehyde is obtained by the action of ferric chloride or of dilute mineral acids upon the electrolytic reduction-products of *m*-nitrobenzaldehyde. It also results when the substance obtained by the action of zinc dust or of amalgamated aluminium upon *m*-nitrobenzaldehyde is exposed to the action of the air, especially in alkaline solution.

EXPERIMENTAL PART.

Conversion of p-Azoxybenzaldehyde into an Oxyazo Compound.

The orange-colored solution of *p*-azoxybenzaldehyde in concentrated sulphuric acid, when heated to 100° and poured into ice-water, yields the unchanged azoxybenzaldehyde. If the temperature be kept at 110° to 120° for some time the solution assumes an intense red color. At the end of an hour and a half the reaction-mixture is poured into cold water. The brown solid which separates out is washed with water and dried on a porous plate. It dissolves in aqueous solutions of ammonia, sodium hydroxide, potassium hydroxide, and alkaline carbonates, forming dark-red solutions. If these solutions come in contact with the skin the latter is dyed yellow. Carbon dioxide, when passed through solutions of the salts, precipitates the brown substance. This dissolves sparingly in alcohol. The alcoholic solution yields, with copper acetate, a brown precipitate which is decomposed by mineral acids. The ammoniacal solution, when treated with an aqueous solution of lead acetate, forms a red, amorphous precipitate. The further investigation of this compound is necessarily interrupted for some months. The reactions indicated are characteristic of the true oxyazo compounds.

Electrolytic Reduction of m-Nitrobenzaldehyde.

The reduction is effected in the same manner as that of *p*-nitrobenzaldehyde.[1] It is reduced with much more diffi-

[1] This JOURNAL, 28, 34.

culty than the latter. The N-*m*-formylphenyl ether of *m*-nitrobenzaldoxime,

,
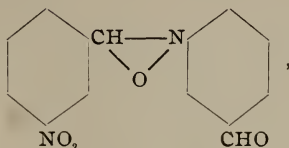
is first formed. By continued reduction this is changed into an insoluble substance, probably an azoxy compound of the formula

$$(ON_2)(C_6H_4.CH\diagup^{O}\diagdown N.C_6H_4.CHO)_2.$$
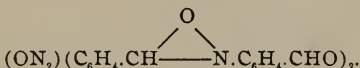
After the current (6 volts, 2 to 3 amperes) has acted six hours a large amount of unchanged *m*-nitrobenzaldehyde remains, together with the primary reduction-product. The filtrate gives no precipitate with sodium carbonate. At the end of fourteen hours the *m*-nitrobenzaldehyde has entirely disappeared and but little of the primary reduction-product remains. In the place of the latter there is a considerable amount of a light-brown, amorphous solid, insoluble in alcohol, acetic acid, and pyridine. This corresponds to the insoluble substance obtained from *p*-nitrobenzaldehyde. In the second case the filtrate yielded a red precipitate with sodium carbonate. The same method that was used with *p*-nitrobenzaldehyde served for the separation of the above crude precipitate into its different components. The *m*-nitrobenzaldehyde dissolved in hot water and was extracted from its aqueous solution by ether. The primary reduction-product, the N-*m*-formylphenyl ether of *m*-nitrobenzaldoxime, dissolves in boiling pyridine, from which the greater part of it separates, on cooling, as a gray, granular solid without distinct crystalline form. The third substance remains undissolved.

Gattermann[1] has shown that *m*-nitrosobenzaldehyde, *m*-nitrobenzaldehyde and a small amount of an unidentified sub-

[1] *Loc. cit.*

stance are formed by the action of ferric chloride upon the N-*m*-formylphenyl ether of *m*-nitrobenzaldoxime. The third substance I have identified as *m*-azoxybenzaldehyde. Bamberger has shown that nitroso compounds react with hydroxylamine compounds to form azoxy compounds. The probable explanation of the formation of azoxyaldehyde in this case is as follows: The ether is oxidized to nitrobenzaldehyde and nitrosobenzaldehyde. The latter reacts with some of the unchanged ether to form azoxybenzaldehyde. The reactions are expressed by the equations:

$$\text{I.} \quad \underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4.CH} \underset{\displaystyle \overset{O}{\diagup\diagdown}}{\text{———}} N.C_6H_4.CHO + O =$$

$$\underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4.CHO} + ON.C_6H_4.CHO ;$$

$$\text{II.} \quad \underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4.CH} \underset{\displaystyle \overset{O}{\diagup\diagdown}}{\text{———}} N.C_6H_4.CHO + ON.C_6H_4.CHO =$$

$$\underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4.CHO} + O \begin{cases} N{\text{—}}C_6H_4.CHO \\ | \\ N{\text{—}}C_6H_4.CHO \end{cases}.$$
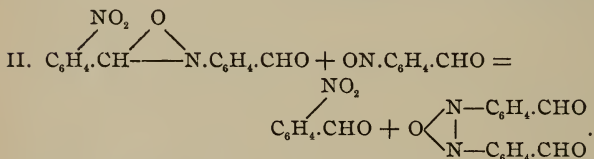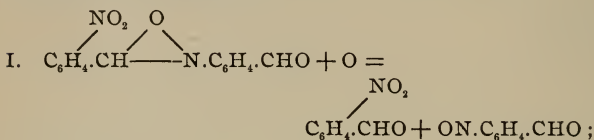
When heated with dilute mineral acids the same ether yields *m*-nitrobenzaldehyde and a small amount of *m*-azoxybenzaldehyde. The first reaction is expressed by the equation

$$\underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4{\text{—}}CH} \underset{\displaystyle \overset{O}{\diagup\diagdown}}{\text{———}} N.C_6H_4.CHO + H_2O =$$

$$\underset{\displaystyle \overset{NO_2}{\diagup}}{C_6H_4{\text{—}}CHO} + HO.HN.C_6H_4.CHO.$$
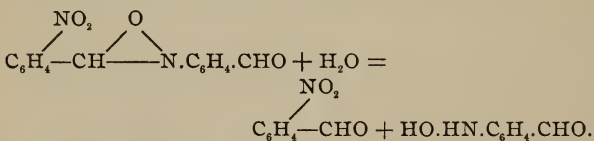
The hydroxylaminobenzaldehyde, so formed, is immediately decomposed by the action of the acid, with or without the participation of the oxygen of the air.

The insoluble secondary reduction-product, when oxidized by ferric chloride, gives *m*-nitrosobenzaldehyde and *m*-azoxybenzaldehyde. The latter alone results when the substance is

boiled with dilute mineral acids. In neither case is *m*-nitrobenzaldehyde to be detected.

m-Azoxybenzaldehyde.—This compound may be prepared by several different methods. It is obtained by treating the primary or the secondary reduction-product of *m*-nitrobenzaldehyde with ferric chloride or with dilute mineral acids. It is obtained most conveniently by the following method : The secondary reduction-product or the crude reduction-product obtained by the prolonged action of the electric current upon *m*-nitrobenzaldehyde, is placed in a round-bottomed flask and treated with a ten per cent solution of ferric chloride. Steam is passed through the mixture until *m*-nitrosobenzaldehyde ceases to pass over. The black, tarry substance remaining in the flask is washed with water to free it from ferric chloride and then repeatedly recrystallized from alcohol with addition of animal charcoal. After the fifth or sixth recrystallization the substance is pure.

When *m*-nitrobenzaldehyde is treated with zinc dust and ammonium chloride solution in the cold a yellowish-brown solution is obtained which, when exposed to the air for a considerable length of time, deposits an amorphous, grayish-yellow solid consisting of more or less impure *m*-azoxybenzaldehyde. If the solution be treated with an aqueous alkali it at once assumes a deep-brown color. The brown color rapidly disappears on shaking the mixture, *m*-azoxybenzaldehyde being formed. This is analogous to the formation of *p*-azoxybenzaldehyde.[1] If the insoluble compound $(C_7H_5NO)_x$, described by Bamberger and Friedmann,[2] be boiled with alcohol and the filtrate be treated with an aqueous alkali, *m*-azoxybenzaldehyde is obtained.

This aldehyde forms almost colorless needles that melt at 129°. It is insoluble in ligroin and cold water, sparingly soluble in ether, hot water, and cold alcohol, but very readily soluble in benzene, acetic acid, and hot alcohol.

[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **28**, 250 (1895).

	Calculated for $C_{14}H_{10}O_3N_2$.	Found. I.	II.
C	66.1	65.7	65.6
H	3.9	4.4	4.5
N	11.0	11.1	...

m-Azoxybenzaldehyde Phenylhydrazone, (ON_2) $(C_6H_4CH:$ $N.NH—C_6H_5)_2$.—This compound is obtained by heating *m*-azoxybenzaldehyde with an excess of phenylhydrazine in alcoholic solution for one hour. Orange-colored crystals separate out. These are filtered out, washed with cold alcohol, and dried on the water-bath. This compound also results by similar treatment of the crude *m*-azoxybenzaldehyde obtained by the zinc dust method. This hydrazone crystallizes in very small, orange-colored needles, melting at 198°.

	Calculated for $C_{26}H_{22}ON_6$.	Found.
N	19.3	19.3

Whether *m*-azoxybenzaldehyde can be obtained from *m*-nitrobenzyl chloride by methods analogous to those used in the preparation of *p*-azoxybenzaldehyde has not yet been determined. Attempts to prepare *o*-azoxybenzaldehyde from *o*-nitrobenzyl chloride were not successful. Bamberger[1] has recently obtained the oxime of the last-mentioned compound by another method.

The further investigation of the azoxybenzaldehydes is still in progress in this laboratory.

UNIVERSITY PLACE, NEBRASKA,
June 20, 1902.

XXII.—CAMPHORIC ACID.

CAMPHANIC AND CAMPHONONIC ACIDS.

[THIRTEENTH PAPER.]

BY WILLIAM A. NOYES AND ROBERT C. WARREN.

The work here described was undertaken for the purpose of securing new evidence as to the structures of camphanic

[1] Ber. d. chem. Ges., **34**, 4023 (1901).

and camphononic acids. While the evidence obtained is mainly of a negative character, several new compounds which seem worthy of a brief description have been prepared.

Hydroxycamphoric Acid.—While camphanic acid,

$$C_8H_{13} \diagdown \begin{matrix} CO_2H \\ CO \\ | \\ O \end{matrix} \quad ,$$
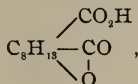
is undoubtedly a lactone, no salt or ester of the corresponding dibasic hydroxy acid has been described. Eleven grams of camphanic acid were heated for twenty-four hours, on the water-bath, with 45 cc. of a 10 per cent solution of sodium hydroxide. By titrating back with nitric acid, using phenolphthaleïn as an indicator, it was found that 96 per cent of the acid had been converted into the sodium salt of hydroxycamphoric acid. The silver salt, $C_{10}H_{14}O_5Ag_2$, was prepared by precipitation and was crystallized from hot water. The salt gave 50.13 per cent silver. Calculated 50.20 per cent.

The *diethyl ester of hydroxycamphoric acid* was prepared from the silver salt by treating it with ethyl iodide and ether. It is a liquid and has an intensely bitter taste. Its specific gravity is 1.0351 at 20°. The rotatory power is $[\alpha]_D = 40°$ at 20° or 39°.6 at 28°.

The analysis gave :

	Calculated for $C_{14}H_{24}O_5$.	I.	II.
		Found.	
C	61.77	62.02	61.76
H	8.82	8.79	8.85

When this work was undertaken it was thought possible by us that the hydroxyl group of this ester was secondary.[1] If this were the case, it should be easy to oxidize it with the formation of the ester of.a ketonic acid. It was found, however, that Beckmann's mixture is practically without effect upon it, while nitric acid converts it into the ester of camphanic acid. This furnishes some confirmation of the accepted view, which is that the hydroxyl group is tertiary.

[1] This JOURNAL, **23**, 133.

Inactive Camphor.

In a previous paper[1] reference was made to an inactive cam-
phor which is now made synthetically from pinene by the Am-
père Chemical Company, of New York. As the method of
preparation is of considerable interest and not easily accessi-
ble, it seems worth while to give the details as given in the
patent.[2] Five parts of dry turpentine (pinene) and one part
of anhydrous oxalic acid are heated to 120° to 130°. There
results a mixture of borneol, borneol oxalate, borneol formate,
camphor, and waste polymerization-products. The esters of
borneol are saponified by heating with milk of lime and the
borneol and camphor are distilled with steam. These are
separated from oily impurities by freezing and centrifugating,
or filtering, and washing. The borneol is oxidized to camphor
by potassium pyrochromate and sulphuric acid and the cam-
phor is further purified.

i-Bromcamphoric anhydride.—Camphoric acid is usually
treated with 2 molecules of phosphorus pentachloride as the
first step in the preparation of bromcamphoric anhydride. As
the first effect is to convert the acid to the anhydride it seems
more rational to start with the anhydride and use but 1 mole-
cule of the pentachloride. The disagreeable evolution of
large quantities of hydrochloric acid mixed with vapors of
phosphorus pentachloride and oxychloride is also avoided.
One hundred grams of camphoric anhydride, 120 grams of
phosphorus pentachloride, and 30 cc. of phosphorus oxychlo-
ride were heated on a water-bath in a flask connected with an
upright condenser till the mass became thoroughly fluid. The
mixture was then cooled, bromine was dropped in, and the
remainder of the operation was conducted as described by
Aschan.

i-Camphanamide, C_8H_{13}—$\begin{matrix} \diagup CON{H_2}^{[3]} \\ CO \\ \diagdown | \\ O \end{matrix}$.—This was prepared by
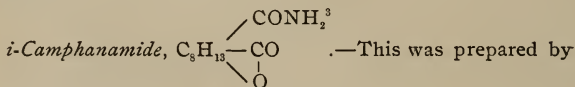
[1] This Journal, **27**, 430.
[2] No. 698,761, April 29, 1902.
[3] Ber. d. chem. Ges., **27**, 3505.

treating *i*-bromcamphoric anhydride with a strong, cold solution of ammonia.[1] The amide crystallizes from alcohol in plates or prisms, which melt at 196°. The active amide melts at 208°.[2]

The analysis gave :

	Calculated for $C_{10}H_{15}O_3N$.	Found.
C	60.91	60.93
H	7.90	7.84

i-Camphononic acid.—This was prepared by the method used by Lapworth and Lenton[3] for the preparation of the active acid, with modification in a few particulars. 19.7 grams of camphanic amide were dissolved in 120 cc. of a 10 per cent solution of sodium hydroxide with the aid of heat. By this treatment it is converted into the half amide of hydroxycamphoric acid, $C_8H_{13} {-} CONH_2$, with CO_2H above and OH below, in which the amide and hydroxyl groups are combined with the same carbon atom.[4] The solution was then cooled to 0° and an ice-cold solution of 5.4 cc. of bromine in 120 cc. of sodium hydroxide was added. The temperature rose spontaneously to 25°. Some nitrogen was also evolved. After standing for an hour the solution was heated on the water-bath for an hour. It was then cooled, acidified with hydrochloric acid, some unchanged amide which separated was filtered off, and the filtrate was evaporated nearly to dryness. This treatment transforms the amide group to the amino group and eliminates the latter with the hydrogen of the hydroxyl group, giving the ketonic acid, $C_8H_{13} {<} {CO_2H \atop O}$. The camphononic acid was extracted with ether, distilled once at a pressure of 15 to 20 mm., and purified by crystallization from a mixture of ligroin and benzene. The yield is poor. The pure, inactive acid melts at 232°.

[1] Auwers and Schnell : Ber. d. chem. Ges., **26**, 1526.
[2] Auwers and Schnell : *Loc. cit.*
[3] J. Chem. Soc. (London), **79**, 1283.
[4] Lapworth and Lenton : *Ibid.*, **79**, 1292.
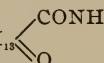
Lapworth gives the melting-point of the active acid as 228°.

The analysis gave:

	Calculated for $C_9H_{14}O_3$.	I.	II.
		Found.	
C	63.53	63.61	63.34
H	8.24	....	8.40

i-Camphononic amide, $C_8H_{13}\Big\langle\begin{matrix}CONH_2\\O\end{matrix}$. — Five grams of

i-camphononic acid were heated on a water-bath with 3.2 grams of phosphorus trichloride till solution was complete. The product was cooled and added gradually to 15 cc. of strong ammonia, cooled to —15°. The precipitate was filtered off, dried, and crystallized from benzene. It melts at 215°.

The analysis gave:

	Calculated for $C_9H_{15}O_2N$.	I.	II.
		Found.	
C	63.90	63.30	63.27
H	8.88	8.89	8.86

It was hoped that by distilling a mixture of *i*-camphononic acid and lime the ketone, $C_8H_{14}O$, recently prepared by one of us with Dr. Patterson,[1] could be obtained. Several grams of the camphononic acid were mixed with twice the weight of lime and the mixture distilled. The distillate possessed the characteristic peppermint-like odor of the ketone, but we did not succeed in securing from it a crystalline oxime.

———

The following compounds have been prepared by methods similar to those used in the preparation of the corresponding active compounds.

i-Camphoric imide, $C_8H_{14}\Big\langle\begin{matrix}CO\\CO\end{matrix}\Big\rangle NH$, crystallizes from water

in needles which melt at 249°. The active imide melts at 245°.

The analysis gave:

[1] This JOURNAL, **27**, 424.

	Calculated for $C_{10}H_{15}O_2N$.	Found.
C	66.30	66.33
H	8.28	8.53
N	7.73	8.25

i-α-Camphoramidic acid, C_8H_{14}⟨$\genfrac{}{}{0pt}{}{CONH_2}{CO_2H}$, was formed chiefly when 36 grams of *i*-camphoric anhydride suspended in 75 cc. of alcohol were treated with ammonia gas. On cooling, the ammonium salt separated, was filtered off, washed with some alcohol, dissolved in water, and decomposed with hydrochloric acid, added carefully to avoid the formation of a gummy precipitate. The acid was purified by dissolving in concentrated hydrochloric acid and precipitating with water. It then melted at 198°. The active acid melts at 175°. The amide group in this acid is that of the secondary carboxyl. 0.1331 gram of the acid took 7.20 cc. of N/10 potassium hydroxide. Theory requires 7.12 cc.

i-Aminolauronic acid, C_8H_{14}⟨$\genfrac{}{}{0pt}{}{CO_2H}{NH_2}$.—The chloride of this acid was prepared exactly as the chloride of the active acid.[1] It melts with decomposition at 266°. The melting-point of the chloride of the active acid is 304°.

The *anhydride* of *i*-aminolauronic acid, C_8H_{14}⟨$\genfrac{}{}{0pt}{}{CO}{NH}$, was prepared by distilling a mixture of the chloride of the acid with twice its weight of lime. It was crystallized from ligroin, in which it is easily soluble. It melts at 209°. The active anhydride melts at 203°.

The analysis gave :

	Calculated for $C_8H_{15}NO$.	Found.
C	70.59	70.82
H	9.81	10.11

i-Nitrosoaminolauronic anhydride, C_8H_{14}⟨$\genfrac{}{}{0pt}{}{CO}{N-NO}$.—One and

[1] This JOURNAL, **16**, 506.

four-tenths grams of the aminolauronic anhydride were dissolved in 140 cc. of water and 8 cc. of concentrated hydrochloric acid, and the calculated amount of sodium nitrite was added. The mixture was allowed to stand for an hour with occasional stirring, the precipitate was filtered off and crystallized twice from water and once from alcohol. It crystallizes in lemon-yellow prisms which melt at 138°.

The analysis gave :

	Calculated for $C_9H_{14}N_2O_2$.	Found.
C	59.34	59.54
H	7.69	7.75

TERRE HAUTE, IND., Oct. 18, 1902.

DERIVATIVES OF PHENYL ETHER. IV.

BY ALFRED N. COOK AND GUY G. FRARY.

In papers previously published accounts were given of the preparation of several derivatives of phenyl ether by the action of orthobromnitrobenzene upon the ortho, meta, and paracresolates of potassium, and reducing, oxidizing, and sulphonating the resulting compounds. During the past few months the work has been continued and extended to the reaction between parabromnitrobenzene and the potassium cresolates, with results as given in this paper and two others that are nearly ready for publication.

4-Nitro-3'-methylphenyl ether, $NO_2\langle\quad\rangle-O-\langle\quad\rangle$ ^{CH_3},
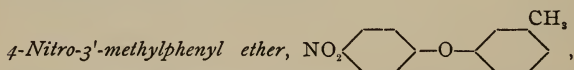
was prepared by the action of potassium metacresolate (prepared as given in a previous paper[1]) on parabromnitrobenzene. Molecular equivalents of the two reacting substances were heated in an oil-bath to 130° when an action began, as was indicated by the ebullition of the fused mass, which continued as long as the temperature was kept at 130°, or above. No rise of temperature was observed due to the reaction itself, as in other cases, but when the containing flask was removed from the bath the reaction ceased. The temperature was

[1] J. Am. Chem. Soc., **23**, 8:0.

kept at 130° to 140° for over two hours, when the reaction seemed to be complete, no action occurring when the temperature was considerably raised. There resulted a copious precipitate of potassium bromide underlying a dark-colored liquid which solidified on cooling. The reaction occurs according to the following equation :

$$NO_2.C_6H_4.Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$
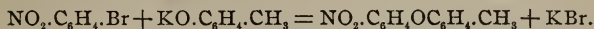
It was not found necessary to extract the substance with ether, wash with caustic soda, and distil with steam, as was done in the earliest work, but it was purified by fractional distillation, directly, under diminished pressure, and then crystallized from hot alcohol, in which it is rather sparingly soluble. The yield was 34 per cent of the theoretical.

4-Nitro-3′-methylphenyl ether is a light-yellow, crystalline substance, which melts at 60° to 61°. It is tasteless but leaves the impression of sulphur when taken into the mouth. Under a pressure of 30 mm. it boils at 230° to 233°. An attempt to oxidize the side-chain by means of chromic acid in acetic acid solution was unsuccessful. The substance was entirely destroyed. Two analyses for nitrogen resulted as follows :

I. 0.3517 gram substance yielded 21.5 cc. N at 23° and 721 mm.

II. 0.3562 gram substance yielded 20 cc. N at 13° and 730 mm.

	Calculated for $C_{13}H_{11}O_3N$.	I.	Found. II.
N	6.11	6.54	6.40

Sulphonic acid of 4-nitro-3′-methylphenyl ether, $CH_3.NO_2.$ $C_{12}H_7.OSO_3H$, was prepared by dissolving some of the corresponding nitromethylphenyl ether in concentrated sulphuric acid by the aid of the heat of the boiling water-bath, diluting with several volumes of water, adding more than sufficient lead nitrate to precipitate the excess of sulphuric acid, precipitating the excess of lead with hydrogen sulphide, and evaporating the solution. When the solution was concentrated to a small bulk the acid separated out as a reddish-yellow, syrupy liquid. When this was dissolved in hot water

and allowed to stand it crystallized out in warty aggregations of fine, white needles. After repeated crystallization it melted at 135°. Some of the salts of the acid were prepared. The composition of the substance was determined by the analysis of the copper salt, given below.

The *barium salt* was prepared by using barium chloride to precipitate the excess of sulphuric acid, instead of the lead nitrate, and sufficient was added also to change all of the sulphonic acid to the barium salt. On concentrating the solution the salt separated out as a fine, white powder. 276.5 parts of the salt are soluble in 1000 parts of water at 80°, and 38 parts are soluble in 1000 parts of water at 24°.

The *strontium salt* was prepared by using strontium nitrate in place of barium chloride, as given above. It was also obtained as a fine, white powder, but it is more soluble than the barium salt.

The *copper salt*, $(CH_3.NO_2.C_{12}H_7O.SO_3)_2Cu + 4H_2O$, was prepared by adding a solution of copper sulphate to a solution of the barium salt in water. The solution of the salt is of a pale-green color. It crystallizes from a water solution in light-green, well-defined crystals. When heated in an air-bath to 100° it loses in weight, as well as its green color, but regains both again by being allowed to come in contact with the air for a short time. On being heated to 160° it changes to a slate color and loses in weight corresponding to 4 molecules of water of crystallization. It is still hygroscopic but does not regain its green color. Two analyses for water and copper resulted as follows :

I. 0.1452 gram salt yielded 0.0160 gram CuO and 0.0134 gram H_2O.

II. 0.1215 gram salt yielded 0.0110 gram H_2O.

	Calculated for $(C_{19}H_{10}O_6NS)_2Cu + 4H_2O$.	Found. I.	Found. II.
Cu	8.48	8.81	....
H_2O(at 100°)	9.58	9.22	9.05

Hydrochloride of 4-amido-3'-methylphenyl ether,
$CH_3.C_6H_4OC_6H_4.NH_2.HCl$, was prepared by reducing 4-nitro-3'-methylphenyl ether in alcoholic solution with zinc and hy-

drochloric acid while warming on the water-bath. The tin was precipitated with hydrogen sulphide and the filtrate evaporated to crystallization. The substance was somewhat difficult to prepare owing to decomposition taking place while evaporating the solution. It crystallizes out in fine, colorless needles, which shrivel at 146°. An analysis for chlorine resulted as follows:

0.0757 gram hydrochloride yielded 0.0466 gram AgCl.

	Calculated for $C_{13}H_{14}NOCl$.	Found.
Cl	15.07	15.19

The *free amide*, prepared by precipitating from a water solution of the hydrochloride with ammonium hydroxide, is stable when dry but partially decomposes while being desiccated. The *hydronitrate*, prepared readily by dissolving the free amide in nitric acid, crystallizes readily in feathery crystals on cooling the solution. The *hydrosulphate*, prepared in the same manner, separated out in fine, white crystals. Both the hydronitrate and the hydrosulphate appeared more stable in our hands than the hydrochloride.

Nitro-4-nitro-3'-methylphenyl Ether, $(NO_2)_2.CH_3.C_{12}H_7O.$— 4-Nitro-3'-methylphenyl ether was treated with concentrated nitric acid in an endeavor to determine its action. On simply mixing the two substances the temperature rose 2° or 3°, and the nitric acid turned to a reddish hue, indicating a slight action at ordinary room temperature. On heating to 90°, however, a violent action began and dense brown fumes of oxides of nitrogen were evolved. The action continued a very few minutes and then ceased. The nitromethylphenyl ether had passed into solution and there remained a dark-red liquid. Continued application of heat apparently did not cause any further action. On pouring this solution into cold water a yellow oil was precipitated which, on repeated washing with water and kneading with a glass rod, became viscous and finally solidified. It was purified by crystallization from alcohol. Nitro-4-nitro-3'-methylphenyl ether is a yellow, crystalline solid which melts at 103° to 104°. The results of the analysis for nitrogen, as well as its mode of formation, would point to its being a dinitromethylphenyl ether.

I. 0.1345 gram substance yielded 13.5 cc. N at 29° and 718 mm.

	Calculated for $C_{13}H_{10}O_5N_2$.	Found.
N	10.22	10.33

MORNINGSIDE COLLEGE,
SIOUX CITY, IA.,
Aug. 22, 1901.

NOTES.

A Rapid Method of Preparation of Crystals of Ammonium Pentasulphide.

By adding to a solution of concentrated ammonium sulphide, which is saturated with sulphur, an equal volume of 95 per cent alcohol I have succeeded in obtaining orange-red, prismatic crystals which form in small rosettes, giving a very beautiful, crystalline formation. The yield is about 60 grams from 200 cc. of ammonium sulphide. The analysis of the crystals was made by the method used by Fritsche[1] and Sabatier[2] with the following results :

I. 0.5595 gram crystals dissolved in HCl gave 0.3052 gram NH_4Cl and 0.3605 gram S.

II. 0.3746 gram crystals gave 0.2040 gram NH_4Cl and 0.2423 gram S.

	Calculated for $(NH_4)_2S_5$.	Found.	
		I.	II.
NH_3	17.35	17.57	17.32
S	65.31	64.43	64.94

Four Carius determinations of total sulphur gave a mean of 81.50 per cent, the calculated amount being 81.63 per cent. The method is so rapid that it suffices to mix the solutions in the evening and set away in a cool place. The crystals are formed by morning. The method will therefore offer an easy way to demonstrate to students of general chemistry the reality of the chemical change involved in the solution of sulphur in ammonium sulphide. Any very wide divergence from the above proportions of alcohol and ammonium sulphide prevents the formation of the crystals.   H. G. BYERS.

UNIV. OF WASHINGTON,
July 18, 1902.

[1] J. prakt. Chem., **32**, 313.
[2] Ann. chim. phys., [5], **22**, 73.

The Calibration of Burettes.

Although various excellent methods for calibrating divided tubes, such as burettes, are in use, an addition to the number of one more, possessing far greater simplicity with at least equal precision, may not be considered a work of supererogation.

The method I have to propose depends upon the fact that if a solid body of known volume be immersed in a liquid contained in a burette, the level of the liquid will rise by an amount determined by the volume of the submerged body and the calibre of the tube. As an immersion body I employ a glass rod (see figure), of about 9 mm. diameter, provided, for convenience sake, with a ring at the top and having a volume of exactly 5 cc. The final adjustment of the volume is easily accomplished by grinding the lower end of the rod until it weighs, when suspended in water at 20° C., 4.987 grams less than when weighed in air. This figure comprises in itself corrections for the buoyant effect of air on weights of brass and on the glass, etc. The immersion-body is suspended from the balance by a fine silk thread or by a fine metal wire, 1 cm. of the latter being immersed. An example will make clear the most convenient mode of procedure in getting the right adjustment. Suppose the partly adjusted body is found to weigh in air 12.7300 grams, and in water of 20° C. 7.7155 grams. This result shows that its present loss of weight on immersion is 5.0145 grams, or 0.0276 gram too great, and that its own apparent weight is 0.0700 gram too great.[1] Hence, if it is ground down till it weighs in air 12.6600 grams, it will have the desired volume of 5 true cc. Of course, for any of the varieties of "conventional" cubic centimeters in use, the constant 4.986 will have to be correspondingly modified.

The apparatus is used as follows : The scrupulously clean burette is filled to the point at which it is desired to begin the calibration with distilled water and shaken so as to wet the sides. Forty-five seconds is allowed for the liquid to run down, and its stand is read. Now the immersion-body is let in, suspended on a fine wire or thread of which 1 cm. is under water, and the level again read. Five cc. minus the difference of the two readings is the required correction. The im-

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[1] If, A = weight in air and W = weight in water, we have

$$\text{Desired weight} = \frac{4.986\ A}{A - W}.$$

mersion-body may now be removed and dried and the entire operation repeated for the succeeding 5 cc. There are no appreciable sources of error beyond those of reading the burette. If the glass is perfectly clear there need be no fear of error from air bubbles adhering to the immersion-body. The method has been used for about two years in this laboratory by myself and many students with much satisfaction.

CHEMICAL LABORATORY OF THE   LAUNCELOT W. ANDREWS.
UNIV. OF IOWA, IOWA CITY,
       January 22, 1902.

A Convenient Gas Generator.

In a recent letter to the editor, Dr. R. M. Bird, of the Mississippi Agricultural and Mechanical College, suggested a very simple apparatus for obtaining a supply of gas for two or three Bunsen burners by saturating air with gasoline vapor. The accompanying cut shows the main features of the apparatus. The air-blast is obtained by means of a filter-pump arranged as shown in Fig. I. The 2-liter bottle should be
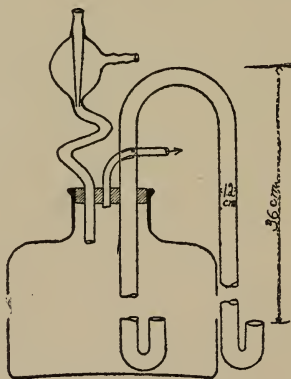
Fig. I.

provided with an outlet tube sufficiently large to prevent flooding the apparatus. If there is not an adequate water supply, a tank may be filled with compressed air by means of a bicycle foot-pump. The saturator, *S*, Fig. II., was made from a broken condenser-jacket, and contained a rolled-up
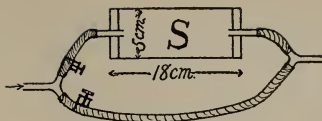
Fig. II.

towel saturated with gasoline. The side tube was added in order to regulate the flow of gasoline to the burner. A single filling with gasoline supplied two burners for a considerable time, giving good-sized, steady flames. A blast-lamp could be used with the apparatus. R. M. BIRD.

REVIEWS.

TEXT-BOOK OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. By G. BUNGE, Professor of Physiological Chemistry at Bâle. Second English edition, translated from the fourth German edition by FLORENCE A. STARLING and edited by ERNEST H. STARLING, M.D., F.R.S., Professor of Physiology in University College, London, England. Philadelphia : P. Blakiston's Son & Co. 1902. 8vo. xi + 470 pp. Price, $3.00 net.

Professor Bunge's lectures on physiological chemistry have had a great influence on physiological chemistry both here and abroad. Representing as they do the ideas which have produced, throughout many years, discoveries of fundamental importance in the school of Schmiedeberg, they have served to spread the method of thought of that school and to render more effective the work of men in other laboratories. These lectures have also the merit of being written by a man who was a philosopher and chemist before he was a physiologist, and who, being thus in a position to grasp the general bearings of his subject, has succeeded in making the dry bones of physiological chemistry interesting even to the beginner.

The author's recommendation to students to go back whenever possible to the original papers is endorsed by the editor, and copious references enable the student to do this very readily. The following statement of the editor will meet the hearty approval of all teachers of physiological chemistry : " A careful study of a few of the classic researches in their original form will do more to acquaint a man with the spirit of physiology than the most arduous perusal of text-books. It is essential to the healthy development of the thinking powers that they should have some work to do, and not be nourished solely on a diet of already digested material."

Professor Bunge is an advocate of the vitalistic theory and occasionally his conclusions are not those which commend themselves to the majority of physiologists. The editor has indicated in foot-notes other opinions and has distinguished such additions by brackets.

The translation is well done and the book is provided with an excellent index. W. R. O.

METHODS OF GAS ANALYSIS. By DR. WALTHER HEMPEL, Professor of Chemistry in the Dresden Techuische Hochschule. Translated from the third German edition and considerably enlarged by L. M. DENNIS, Professor of Analytical and Inorganic Chemistry in Cornell University. New York : The Macmillan Co. 1902. Price, $2.25.

The great value of this book as a guide in all gas analysis is so well recognized that it is only necessary to call attention to the publication of this edition which '' has been thoroughly revised by both the author and the translator, and has been changed to such an extent that this translation may indeed be regarded as a fourth edition of the book.''

'' The additions comprise several new methods of collecting and keeping gas samples ; determinations with the Honigmann, Bunte, and Orsat apparatus ; the new Hempel methods for exact gas analysis ; new methods for the determination of combustible gases ; the separation of argon from the atmosphere ; improved methods for the determination of carbon monoxide in gas mixtures ; the analysis of acetylene gas ; the examination of gases produced by living bacteria ; the simultaneous determination of fluorine and carbon dioxide ; the determination of the heating power of gases ; sulphur in organic substances ; the gas lantern ; the volumetric determination of carbon in iron ; the analysis of gases evolved in the electrolysis of chlorides and in the manufacture of bleaching-powder, together with many minor changes and additions throughout the book.'' J. E. G.

Corrections.

Page 4, line 7. For ''*base*'' read ''*bore*.''
Page 13, line 2 from bottom. For ''*collar*'' read ''*ring*.''

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